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ON
INORGANIC AND THEORETICAL CHEMISTRY

BY
J. W. MELLOR, D.Sc., F.R.S.

VOLUME XV

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ABBREVIATIONS

aq. = aqueous

atm. = atmospheric or atmosphere(s)

at. vol. = atomic volume(s)

at. wt. = atomic weight(s)

T° or °K = absolute degrees of temperature

b.p. = boiling point(s)

θ° = centigrade degrees of temperature

coeff. = coefficient

conc. = concentrated or concentration

dil. = dilute

eq. = equivalent(s)

f.p. = freezing point(s)

m.p. = melting point(s)

$\text{mol(s)} = \begin{cases}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{cases}$

$\text{mol(s).} = \begin{cases}\text{molecule(s)}\\ \text{molecular}\end{cases}$

mol. ht. = molecular heat(s)

mol. vol. = molecular volume(s)

mol. wt. = molecular weight(s)

press. = pressure(s)

sat. = saturated

soln. = solution(s)

sp. gr. = specific gravity (gravities)

sp. ht. = specific heat(s)

sp. vol. = specific volume(s)

temp. = temperature(s)

vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5**. 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances A, B, and C, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the

triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

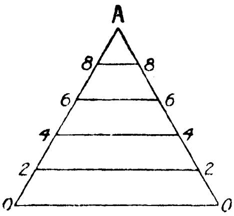

FIG. 1.

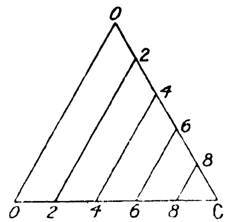

FIG. 2.

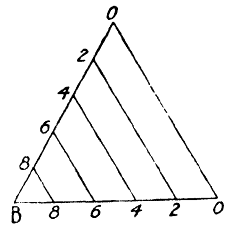

FIG. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

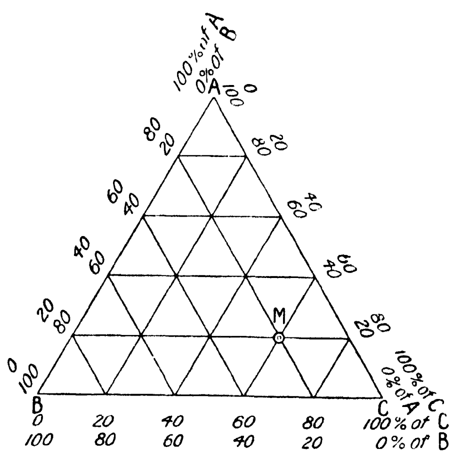

FIG. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

CHAPTER LXVIII

NICKEL

§ 1. The History of Nickel

THE mineral *kupfernickel* described by U. Hiärne,[1] in 1694, has the appearance of a copper ore, but not the smallest particle of copper can be extracted from it. According to F. X. M. Zippe, the word " nickel " appears to have been used amongst the miners as a *Schimpf* name, that is, a disparaging or derogatory term derived maybe from Nikolaus ; if so, then, as suggested by A. G. Charleton, the term " kupfernickel " might be translated " *Old Nick's copper,*" and so J. Woodward called it *cuprum nicolai*. We are told—*vide* cobalt—that the mediæval Saxon miners working the silver ores encountered minerals which had the appearance of good silver ores, but, when smelted, emitted a disagreeable smell, and yielded no silver. The miners concluded that these ores were bewitched by the Nixes and Cobolds that dwelt underground. The objectionable minerals were thrown on to the waste-heaps, and called contemptuously *Nixes' ore* and *Cobolds' ore*. Centuries afterwards these minerals were found to be the arsenides of two new metals, and the names of the metals, cobalt and nickel, are thus derived from a mediæval superstition. The history was discussed by W. H. Baldwin.

The mineral has been previously discussed—**9.** 51, 10—as *niccolite*, its modern cognomen. The idea that kupfernickel is a copper compound seems to have prevailed at the end of the seventeenth and beginning of the eighteenth century, for in 1726, J. H. Linck said that it is a cobalt ore mixed with copper ; and J. G. Wallerius, that it is a copper-red ore consisting of cobalt, iron, and arsenic. Analogous views were held by J. A. Cramer, J. F. Henckel, and C. von Linnæus in the first half of the eighteenth century.

In 1751, A. F. Cronstedt [2] published in Stockholm a report of his examination of some ores in the cobalt mines of Helsingland, Sweden. When the earth under examination was weathered, it acquired a green crust, which furnished long crystals of a green sulphate or vitriol. When the sulphate was calcined, it furnished a grey calx, or colcothar, which when reduced yielded a yellowish, hard, brittle metal with a white fracture. The metallic part of the vitriol furnished with borax a brown glass. He therefore inferred that the earth contained in addition to iron and cobalt a new semi-metal. When the soln. of the semi-metal in acid was treated with a fixed alkali, it yielded a greenish-white precipitate free from copper. A. F. Cronstedt then showed that the new semi-metal was the dominant base in kupfernickel, and he accordingly retained the affix of reproach—**nickel**—for the new semi-metal. He found that the kupfernickel of Freiberg contained arsenic, sulphur, nickel, and iron ; and that the speiss obtained in the preparation of smalt contained a relatively large proportion of nickel. Nickel or nickel calx was found to unite readily with sulphur, forming a yellow compound which when roasted furnished nickel calx. Nickel forms a hard, white alloy with copper, which, unlike nickel free from copper, forms in the borax bead a green glass, and a soln. of the alloy in acid gives a precipitate of copper when treated with zinc or iron. These facts were considered to demonstrate that nickel itself is free from copper.

Most chemists accepted A. F. Cronstedt's nickel as a new element, but, as T. Bergman stated, some—*e.g.*, B. G. Sage (1772), and A. G. Monnet (1775)—

"were led rather by vague conjecture and specious appearance than by satisfactory experiment," and retained the old opinion that kupfernickel is a compound of iron, copper, cobalt, and arsenic. They also considered cobalt and nickel to be the same element. T. Bergman then examined the new element with the idea of finding if the characteristics of A. F. Cronstedt's nickel were sufficient to establish its right to recognition as an element *sui generis*. T. Bergman concluded that whilst with the knowledge then available "it was not possible to obtain a perfect and complete purification of nickel from all heterogeneous mixtures," sufficient was known to establish the right of nickel to recognition as a metal with distinct properties of its own which persist in all its combinations. He added:

Vague suspicions that nickel, cobalt, and manganese can be generated from iron because of the difficulty involved in preparing the metals free from iron, must give way to phenomena and properties which are constant, and the metals themselves must be regarded as of an origin altogether distinct and peculiar to themselves. There is no doubt that many well-known metals, acknowledged to be distinct substances, would not endure more severe trials than does nickel. . . . If the genesis of natural productions is to be established by fanciful metamorphoses, the whole truth and certainty of natural philosophy must soon be overturned. So long as plausible conjectures are substituted for opinions formed on the sure basis of experiment, we shall always embrace the shadow for the substance.

N. Leblanc raised some objections to T. Bergman's conclusion that nickel is a chemical individual *sui generis*, but the work of J. L. Proust, J. B. Richter, L. J. Thénard, and R. Tupputi removed all doubts, and since that time nickel has occupied a place in the list of elements. The history of nickel has been discussed by M. E. Weeks, D. F. Hehnemann, W. H. Baldwin, R. Kirwan, and F. Kapff.

The work of G. Krüss and F. W. Schmidt led them to attribute the anomalous positions of nickel and cobalt in the periodic table to the presence in ordinary nickel and cobalt of an unknown, foreign element which was named *gnomium*, but this opinion was not supported by the work of C. Winkler, L. Mond and co-workers, P. Schützenberger, and T. W. Richards and A. S. Cushman. A new element was reported by L. C. von Vest to be present in nickel ore, and he proposed to call it *junonium* or *sirium*, whilst L. W. Gilbert suggested *vestäium* or *vestium*, but the alleged element was shown by M. Faraday to be a mixture of nickel, iron, sulphur, and arsenic. T. Dahll reported a new element—named *norwegium*—in gersdorffite, but the report has not been confirmed.

The analysis of the early Chinese alloy, *packfong*, by G. von Engeström, in 1776; and the analyses of Bactrian coins, probably 200 B.C., by W. Flight, and A. G. Charleton, show that, at these remote periods, the ores employed for making coinage metal contained some nickel—*vide infra*, the copper-nickel, and the copper-nickel-zinc alloys. In 1777, J. C. F. Meyer noted that a Siberian meteorite when treated with sulphuric acid gave a green soln. which became blue when treated with ammonium chloride, but J. L. Proust, in 1799, is generally considered to have been the first to demonstrate the presence of nickel in meteoritic iron—*vide infra*, nickel-iron alloys.

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§ 2. The Occurrence of Nickel

According to K. Kraut,[1] and T. Carnelley, nickel is much more widely distributed in nature than was formerly supposed, it is closely allied to cobalt, and the two elements are almost always associated with one another and with iron. According to V. M. Goldschmidt, during the cooling and solidification of the earth, the molten mass separated into three layers—a metallic layer, a sulphide layer, and a silicate layer—*vide* iron. The occurrence of the two metals cobalt and nickel in association with iron was supposed to form the central core of the earth, and, from the analogy with meteoric iron, it is possible that the iron in the central core contains 6 to 10 per cent. of nickel, and that the proportion of nickel and cobalt is approximately as 15 : 1. The terrestrial minerals awaruite and josephinite represent native nickel. The cobalt and nickel in the sulphide layer, (Fe, Ni, Co)S, amount to 1 to 4 per cent. Nickel is thus a primary constituent of many sulphides, arsenides, antimonides, and tellurides. Nickel has been frequently detected in igneous rocks, and F. W. Clarke noticed that nickel is specially characteristic of magnesian igneous rocks, where it is generally associated in them with chromium. Nickel also occurs primarily in silicate rocks. P. Pondal observed that the proportion of nickel in basic rocks is greater than in acidic rocks, where the proportion is low or zero; in fifteen samples of Galician magmas, he found 0·0 to 0·42 per cent. of NiO. The subject was discussed by J. H. L. Vogt.

According to F. W. Clarke, nickel is distributed more abundantly than copper, for whilst the igneous rocks of the earth's crust contain approximately 4·56 of iron to 0·02 of nickel, the proportion of copper is about 0·010, and the proportion of the common metals, zinc and lead, is still less. According to F. W. Clarke and H. S. Washington, the relative abundance of nickel in the igneous rocks of the earth's crust is 0·020 when that of cobalt is 0·001, and that of iron is 5·01 per cent. J. H. L. Vogt gave 0·005 per cent. for nickel; W. Vernadsky gave 0·01; G. Berg, 0·018 per cent.; and F. W. Clarke, 0·0274 per cent. of oxide. W. and J. Noddack and O. Berg gave 3×10^{-5} for the absolute abundance of nickel when that of cobalt is 3×10^{-6} and that of iron, 10^{-2}. A. E. Fersmann calculated 0·0029 for the percentage number of atoms of nickel in the earth's crust. The general subject was discussed by K. Kraut, E. Dittler, G. Berg, P. Niggli, G. Tammann, E. Herlinger, O. Hahn, W. Lindgren, J. Joly, and A. von Antropoff.

According to A. Terreil,[2] the metal occurs associated with the magnetic platinum ores of Nischne-Tagilsk, Urals; whilst T. Petersen found it in the magnetic iron of Pregattin, Tyrols; A. Sella, alloyed with 26·6 per cent. of iron in the sands of

Elvo, Piemont; and R. A. A. Johnston, in the sands of Yukon. Some native alloys of iron and nickel have received special names—**awaruite,** $FeNi_2$, observed by W. Skey in Awarua Bay, New Zealand; **josephinite,** Fe_2Ni_5, by W. H. Melville, in the placer sands of Josephine and Jackson Counties, Oregon, and by G. S. Jamieson, in the sands of Smith River, California; **souesite,** $FeNi_3$, by G. C. Hoffmann, in the sands of Frazer River, British Columbia; **octibbehite,** Fe_2Ni_3, by W. J. Taylor in Octibbeha, Missouri; and **catharinite,** Fe_2Ni, by S. Meunier, from Santa Catharina, Brazil—*vide infra*, the iron-nickel alloys. E. Casoria, and G. Paris observed nickel amongst the products of the Vesuvian eruption of 1906. The occurrence of extra terrestrial nickel in meteorites is discussed in connection with the iron-nickel alloys, and in connection with extra terrestrial iron. The first definite proof of the presence of nickel in meteorites was made in 1799 by J. L. Proust. G. Berg, and E. Herlinger gave 1·53 per cent. for the average nickel content of stony meteorites, and 8·51 per cent. for iron meteorites. G. P. Merrill estimated that the analyses of meteorites published up to 1916 showed that meteorites contained 1·15 per cent. of metallic nickel, and 0·48 per cent. of oxide—eruptive terrestrial rocks contained 0·025 per cent. of nickel oxide. J. and W. Noddack's estimates of the percentage atomic distribution relative to oxygen unity are:

Earth's crust	Igneous rocks	Meteoric iron	Troilite	Atomic distribution
$1{\cdot}8\times10^{-4}$	$2{\cdot}01\times10^{-3}$	$8{\cdot}46\times10^{-3}$	$2{\cdot}88\times10^{-2}$	$4{\cdot}2\times10^{-2}$

The subject was discussed by H. von Klüber, O. C. Farrington, F. Behrend and G. Berg, G. P. Merrill, J. and W. Noddack, W. Crookes, etc.—*vide* iron. G. Kirchoff, A. J. Angström, A. Cornu, and J. N. Lockyer obtained spectroscopic evidence of the existence of nickel in the sun. Confirmatory observations were made by A. Cornu, H. A. Rowland, H. von Klüber, F. Behrend and G. Berg, H. N. Russell, H. M. Vernon, S. A. Mitchell, F. McClean, G. E. Hale and W. S. Adams, and A. de Gramont. A. Albrecht observed nickel lines in the spectrum of Germinorum; and H. M. Pillans, in that of β-Lyræ. The occurrence of nickel lines in stellar spectra was discussed by H. von Klüber, C. J. Kreiger, W. W. Morgan and G. Farnsworth, O. Struve and P. Swings, G. P. Merrill, J. Stebbins, W. C. Rufus, G. E. Hale and co-workers, C. D. Shane, F. J. M. Stratton, and J. Storey. F. S. Hogg reported the spectral lines of nickel in comets.

Native nickel occurs in nature alloyed with iron in meteorites, and in a few terrestrial minerals, but the native element is a curiosity of no industrial importance. Workable deposits of nickel are rare; the most important deposits occur in Ontario, Canada, and in New Caledonia. These deposits control the world's market for the metal. The useful ores of nickel furnish three classes:

(i) *Sulphides—e.g.*, pentlandite, polydymite, linnæite, and millerite. The sulphide ores accompanying pyrrhotite and chalcopyrite are always associated with a subsilicic rock like norite, peridotite, and sometimes diabase or diorite. The ores are usually at or near the margin of laccoliths, and are partly massive metal sulphides, and partly disseminated in the marginal zone of the rock. The Sudbury, Ontario, deposits, for example, occur in an enormous laccolith which occupies the interior of a basin-like depression, and it is overlaid with a considerable thickness of sedimentary and pyroclastic rocks. Two main theories have been proposed to explain the origin of the Sudbury deposits: (*a*) the igneous or magmatic segregation theory assumes that the nickel, copper, and iron sulphides cooled and segregated from a molten state like the igneous rocks; and (*b*) the hydrodeposition theory assumes that the ores have been deposited from hot aqueous solutions circulating along zones of crushing and faulting. The theory that the Sudbury ores were produced by molten injections which solidified in the fissures as veins, etc., is favoured by R. Bell,[3] J. W. Gregory, C. F. Tolman and A. F. Rogers, J. F. Kemp, J. H. L. Vogt, W. Campbell and C. W. Knight, D. C. Davies, H. B. von Foullon, T. L. Walker, A. P. Coleman. A. E. Barlow, etc. D. H. Browne observed that in

the cooling of a copper-nickel matte, the copper sulphides favour the margins of the mass, and the nickel sulphides concentrate near the centre, and the sulphides at Sudbury are similarly distributed. In the alternative theory advocated by R. Beck, W. G. Miller, C. W. Dickson, and W. Campbell and C. W. Knight, it is assumed that the ores were formed by the circulation of heated waters containing a soln. of the components of nickel, copper, and iron sulphides, and, to a minor extent, lime, magnesia, silica, etc. The nickel, copper, and iron sulphides were then precipitated as pentlandite, chalcopyrite, and pyrrhotite. E. Weinschenk considered that the nickeliferous pyrrhotites of southern Schwarzwald are not magmatic. Synthetic experiments show that these minerals may be formed by both dry and wet processes. The origin of nickel ores was also discussed by A. M. Bateman, E. R. Bush, S. St. Clair, F. W. Clarke and C. Catlett, J. H. Collins, W. H. Collins, M. A. Dresser, J. Garnier, W. H. Goodchild, H. M. Roberts and R. D. Longyear, L. P. Silver, and T. L. Walker.

(ii) *Arsenides—e.g.*, niccolite and chloanthite. F. Gillman considered the niccolite deposits in the serpentine of Malaga, Spain, to be magmatic. The arsenide ores of Cobalt, Ontario, occur in narrow veins cutting metamorphosed, fragmental, pre-Cambrian rocks which have been intruded by a high mass of dolerite. The vein also contains barytes, fluorspar, dolomite, and quartz, all typical of minerals deposited from aq. soln. W. G. Miller considered that the mineralization was produced by magmatic waters which accompanied or followed the dolerite eruption. F. W. Voit considered that the arsenide ore of Dobschau, Hungary, was deposited from circulating soln. The arsenides occur in a carbonate gangue at or near contacts of diorite. C. R. Keyes discussed metasomatic replacements in limestone; and the oxidation or carbonation of sulphides and arsenides of nickel and cobalt was discussed by J. F. Kemp, F. Gillman, etc.

(iii) *Hydrated silicates—e.g.*, garnierite, genthite, connarite, and nepouite—found in New Caledonia; Riddles, Oregon; North Carolina; Revda, Urals; Frankenstein, Silesia; and Mount Avala, Serbia. These silicates have a more or less indefinite composition. They occur in weathered zones of basic igneous rocks—*e.g.*, peridotites—and are frequently altered to serpentine in which the contained nickel is considered to have been a primary constituent. In some cases, during the weathering, the nickel minerals were dissolved and deposited from soln. in shrinkage cracks and seams, and in brecciated portions of the mother rock. These minerals were discussed by W. L. Austin, A. E. Barlow, H. J. Riddle, F. W. Clarke, H. B. von Foullon, G. F. Kay, J. S. Leckie, D. Levat, W. Schornstein, A. Liversidge, E. Dittler, and F. D. Power.

Nickel occurs as an essential or accessory constituent of many minerals, but workable deposits are comparatively rare. The chief nickel minerals are as follow:

Aarite, or **arite,** an antimonial nickel arsenide. **Alipite,** an impure hydrated nickel silicate. **Annabergite,** $Ni_3(AsO_4)_2.8H_2O$. **Awaruite,** $FeNi_2$. **Badenite,** $(Co,Ni,Fe)_2(As,Bi)_3$. **Beyrichite,** Ni_3S_4, or $2NiS.NiS_2$. **Black nickel,** *vide* nicomelane. **Blueite,** a nickeliferous pyrite approximately $NiS_2.12FeS_2$. **Bravoite,** a nickeliferous pyrite. **Breithauptite,** NiSb. **Bunsenite,** NiO. **Cabrerite,** $(Ni,Mg)_3(AsO_4)_2.8H_2O$. **Catharinite** or **catarinite,** Fe_2Ni. **Chathamite,** a variety of chloanthite. **Cheleutite,** a nickeliferous smaltite, **Chloanthite,** $NiAs_2$. **Cobalt nickel pyrite,** $(Fe,Co,Ni)S_2$. **Connarite,** $H_4Ni_2Si_3O_{10}$. **Copper nickel,** *vide* niccolite. **Corynite,** a form of gersdorffite with part of the arsenic replaced by antimony. **Desaulesite,** a hydrated silicate of zinc and nickel associated with chloanthite. **Emerald nickel,** *vide* texasite. **Folgerite,** a form of pentlandite. **Forbesite,** $(Ni,Co)HAsO_4.4H_2O$. **Garnierite,** $(Ni,Mg)SiO_3.nH_2O$. **Genthite,** $H_4Mg_2Ni_4(SiO_4)_3.4H_2O$, or $(Mg,Ni)_2Si_3O_8.nH_2O$. **Gersdorffite,** Ni,AsS. **Gunnarite,** a form of pentlandite. **Hauchecornite,** possibly $(Ni,Co)_7.(S,Bi,Sb)_8$. **Heazlewoodite,** a form of pentlandite. **Hengleinite,** $(Co,Ni,Fe)S_2$. **Heubachite,** $3(Co,Ni,Fe)_2O_3.4H_2O$. **Horbachite,** $(Fe,Ni)_2S_3$, or $4Fe_2S_3.Ni_2S_3$. **Josephinite,** Fe_2Ni_5. **Kallilite,** NiBiS, or $NiS_2.NiBi_2$. **Kerzinite,** a peat containing nickel silicate. **Kupfernickel,** old name for niccolite. **Lawrencite,** $(Fe,Ni)Cl_2$. **Lillhammerite,** pentlandite. **Lindackerite,** $Ni_3Cu_6(OH)_4SO_4(AsO_4)_4.5H_2O$. **Linnæite,** $(Ni,Co)_3S_4$. **Maucherite,** Ni_4As_3 or Ni_3As_2. **Maufite,** a silicate of nickel, aluminium, etc. **Melonite,** Ni_2Te_3. **Millerite,** NiS. **Morenosite,** $NiSO_4.7H_2O$. **Nepouite,** $(Ni,Mg)_3Si_2O_7.2H_2O$. **Niccolite,** NiAs. **Nickel bloom,** or

annabergite. **Nickel glance,** gersdorffite. **Nickel green,** or annabergite. **Nickel-gymnite,** a gymnite with part of the magnesium replaced by nickel as in genthite. **Nickel ochre,** or annabergite. **Nickel smaragd,** or zaratite. **Nickel stibine,** or ullmannite. **Nickel-skutterudite,** (Ni,Co,Fe)As_3. **Nickeline,** NiAs. **Nicomelane,** Ni_2O_3. **Nicopyrite,** pentlandite. **Noumeaite,** or **noumeite,** a dark green form of garnierite which is usually pale green. **Numite,** or noumeite. **Octibbehite,** Fe_2Ni_3. **Pentlandite,** (Ni,Fe)S. **Pimelite,** an impure hydrated nickel silicate. **Placodite,** or **plakodine,** a form of maucherite. **Polydymite,** Ni_4S_5. **Pyromelane,** *vide* moresonite. **Rammelsbergite,** (Ni,Co,Fe)As_2. **Rewdanskite,** $(Ni,Mg,Fe)_3Si_2O_7.2H_2O$. **Röttisite,** $Ni_2Si_3O_8.2H_2O$. **Safflorite,** (Co,Ni,Fe)As_2. **Saynite,** a mixture of polydymite and bismutite. **Smaltite,** (Co,Ni,Fe)As_2. **Souesite,** $FeNi_3$. **Spathiopyrite**—safflorite. **Temiskamite,** Ni_4As_3. **Texasite,** $3NiO.CO_2.5H_2O$. **Transvaalite,** an impure nickeliferous, arsenical, cobalt silicate. **Trevorite,** $NiO.Fe_2O_3$. **Ullmannite,** NiSbS. **Villamaninite,** $(Cu,Ni,Co,Fe)(S,Se)_2$. **Violarite,** a copper nickel sulphide. **Whartonite,** a nickeliferous pyrite. **White nickel,** *vide* chloanthite. **Williamite,** (Ni,Co)SbS. **Willyamite,** $(Ni,Co)S_2Sb_2$. **Winklerite,** an impure cobalt, nickel arsenate. **Wolfachite,** Ni(As,Sb)S. **Zaratite,** $Ni(OH)_2\{Ni(OH)\}_2CO_3.4H_2O$.

The sulphide ores are represented by the pyrrhotite-chalcopyrite ores of Sudbury, and Norway. Similar ores have been mined to a relatively small extent in Pennsylvania, Tasmania, Sweden, Italy, South Africa, etc. The sulphides associated with the lead ores of south-east Missouri have also been worked for cobalt and nickel. The arsenical ores have been worked for cobalt and nickel in Saxony, Bohemia, France, and principally at Cobalt, Ontario. Silicate and oxidized ores have been worked in Greece, Madagascar, North Carolina, Oregon, and principally in New Caledonia. Before the opening of the New Caledonia mines, mines were operated in Norway, Sweden, Germany, Austria, and Italy. Norway was the largest producer up to 1877, when she was eclipsed by New Caledonia. The mine at Lancaster Gap, Pennsylvania, began to produce nickel about 1863, but it had to close down in 1891 owing to competition with the richer deposits of New Caledonia, and Sudbury. Since the advent of the New Caledonian ore in 1875, and of the Sudbury ore in 1886, other sources of supply have become relatively insignificant. Basic igneous rocks in many parts of the world contain sufficient nickel to make them of economic value, but other poorer deposits are not likely to be seriously exploited so long as the deposits like those at Sudbury are available.

The map, Fig. 1, summarizes the geographical distribution of the principal deposits of nickel. There are many general reports on the occurrence of nickel ores.[4]

Europe.—In **Great Britain,**[5] a number of deposits have been reported and in some cases worked, but to-day these deposits are of no economic value. W. Borlase, in 1758, noted the occurrence of nickel at Peengreepju Gwennap; and, according to W. G. Rumbold, niccolite was raised at the Pengelly mine, St. Ewe. Nickel and cobalt ore was also raised from St. Austell Consols, Fowey Consols, and East Pool mines between 1854 and 1861. Other deposits in Cornwall have been reported at Dolcoath, and other mines in the Camborne and Illogan districts. Pentlandite has been found in the Wheal Jane mine, Truro; niccolite, in the South Tresavean mine; millerite, at Wheal Spavnon; and nickel, silver, copper and uranium ores as well as pyrite in the Roskrow-United mines, Ponsanooth. Millerite occurs in the clay ironstones of the South Wales Coal Measures—*e.g.*, at Merthyr Tydfil; and nickel minerals occur associated with the iron ores at Moel Hiraddug, Cwm, Flintshire. Zaratite occurs at Warren Carr, Darley Dale, Derbyshire. Pentlandite was mined at Gille-Braghad near Inverary, in Scotland, between 1854 and 1867. There is also a deposit at Craignure near Inverary; and nickeliferous pyrrhotite occurs near Palnure Burn, Kirkcudbrightshire. The mining of niccolite at Hilderstone, Linlithgowshire, has been conducted in a desultory way between 1606 and 1873. In **France,**[6] there are no known nickel deposits of any commercial importance. There are small deposits at Chalanches, Dauphine. These ores were first worked for silver, and the slags were afterwards treated for nickel and cobalt. In **Portugal,**[7] there are nickeliferous ores at Mirando do Corvo. In **Spain,**[8] there are deposits of nickel in the serpentines of Malaga. Some garnierite in Los Jarales near Carratraca was mined for a time, but could not compete with the New Caledonian ore. There are also similar ores in the Sierra Alpujata near Ojen. In **Italy,**[9] there are small unimportant deposits at Varallo in Piedmont in the Lake Maggiore district, but they have yielded little ore on a commercial scale. In **Switzerland,**[10] nickel and cobalt ores are said to occur in the Gollyre and Grand Praz mines near Ayer, Val d'Anniviers; and at Kaltenburg, Turtmanntal. In **Germany,**[11] a few deposits of nickel are known but none is of any economic importance. There are deposits of the garnierite type near Frankenstein, Silesia; there is a deposit at Aeussert,

Sohland; Steben and Lichtenberg in Bavaria; Horbach in the Black Forest; and near Dillenburg, Nassau. The once-famous cobalt deposits of Schneeberg and Annaberg have yielded small quantities of nickel. In **Austria,**[12] there are mines on the Nöckeberg, near Leogang, and at Mitterberg in the Salzburg Alps; the Leo lode near Salzburg and in the Kitzbühel district in the Tyrol. In **Czechoslovakia,**[13] there are small deposits in the Joachimsthal district, and at Schluckenau in Bohemia; and at Dobschau in the Deptau mountains, formerly in Hungary. In **Yugoslavia,**[14] no important nickel deposits have been discovered. Small deposits of millerite have been found in the Mount Avala lead mines; in the Zavlaka zinc-lead deposits; and at Sadyevats near Ivanjitsa. In **Sweden,**[15] small deposits occur at Klefva, Smäland; Kusa, Dalarne; and at Ruda, Ostergötland. In **Norway,**[16] about 40 deposits of nickel ore are known—*e.g.* at Skorovas, near Trondhjem, the Lillebjeldklumpen mine near Lake Tunsjö; Flaad mine in Sätersdäl; the Fasco mine near Haugesund; and the Ertch mine near Ringerike. In **Finland,**[17] at Petsamon. In **Russia,**[18] there is a deposit of the garnierite type at Reodinsk in the Urals; in the Nijni-Karkadinsk mine, the Khudyakoosk mine, the Staro-Cheremshansk mine, and the Tunkinsk mine in the Urals. In **Greece,**[19] there are nickel ores of the garnierite type, and also chromiferous iron ores containing nickel—on the islands Eubœa, and Skyros of the Greek Archipelago; the districts of Locris and Bœotia.

Asia.—In **Siberia,**[20] north-east of Balkash land. In **Asiatic Turkey,**[21] an occurrence of nickel ore at Kastamuni; and there is also one at Aidin. In **India,**[22] nickeliferous pyrrhotite has been reported in various places in Rajputana; in the reefs of

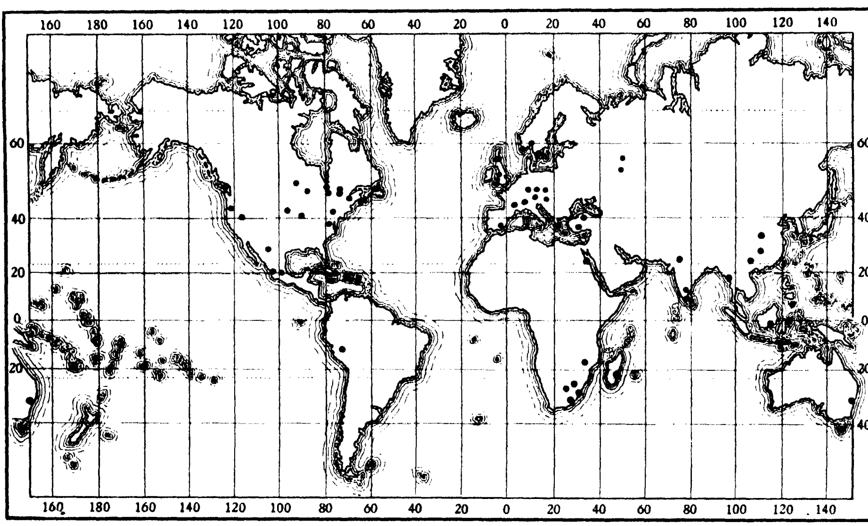

FIG. 1.—The Geographical Distribution of the Nickel Ores.

Kolar; and in the pyrite of the Henzada district, Burma. There are also complex sulphide ores in Tobala, South Travancore. In **Dutch East Indies,**[23] there is a deposit of nickeliferous, chromiferous iron ore on Sebuku Island off the coast of Borneo. Nickeliferous iron ore of the lateritic type has been reported north of Malili, in Celebes.[24] In **China,**[25] there are nickel ores south-east of Yun-nan; in the Tungchwan district; in the Red River district west of Kochiu; near Wei-ning, north-west of Kwei-chow; and in Shen-si. The alloy packfong has been used for a long time in China for domestic utensils, and it was made from a nickeliferous copper ore mixed with tin, lead, and zinc. In **Japan,**[26] the Natsume nickel deposits were formerly worked. In the **Philippine Islands,**[27] there is chromiferous iron ore on the island of Mindanao. In **New Caledonia,**[28] the deposits of garnierite are of second importance to the Sudbury deposits. They were discussed by J. Garnier in 1865.

Africa.—In **Egypt,**[29] there is a deposit of the silicate type on St. John's Island in the Red Sea. In **Abyssinia,**[30] nickel and copper ores have been found in the Walaga Province. In **Madagascar,**[31] there are nickel ores of the garnierite type. There is one deposit at Valzoro near Amboutra, in the province of Fianarantsoa; and another deposit near Ambatondrazaka, on the Ombe River. In **Nyasaland,**[32] there is a deposit of nickeliferous pyrrhotite in the Blantyre district. In the **Union of South Africa,**[33] there is a deposit of nickeliferous pyrrhotite at Insizwa, Cape Province; a deposit at Blauwbank, Transvaal, and at Vlakfontein in the Rustenburg district. There are also deposits at Derde Geld, Lydenburg; and near the Sheba Bridge, Barberton district. In **Natal,**[34] there is an occurrence of the garnierite type in the Nkandhla district, Zululand.

North America.—In **Canada,**[35] there are numerous deposits of nickel, but only the

nickeliferous pyrrhotite deposits about *Ontario* have been worked. The largest and richest known deposits in the world occur on the north side of Lake Huron, in the Sudbury region. The ores here are of two types—*marginal deposits* occur at the basal margin of the norite lying between it and the adjoining rock; and *offset deposits* are connected on the basic edge of the norite intrusion by dyke-like projections. There are also deposits in Dundonald near Matheson; near Shebandowan Lake; and near Nairn Centre, south of Worthington. Nickel also occurs as a minor constituent of the complex silver-cobalt ores of Cobalt, Ontario. In *British Columbia*, there is an occurrence on the Jordan River, Vancouver Island; in *New Brunswick*, at St. Stephen; in *Manitoba*, in the Maskwa River area, and in the Oiseau River area; and in Quebec, there are deposits in Orford, and Calumet. In **Newfoundland**,[36] there are sulphide ores associated with the Tilt Cove copper ores. In the **United States**,[37] only a few nickel deposits are known, and these are not of much economic importance. Some nickel has been obtained as a by-product from the smelting of the lead ores of *Missouri*. There are sulphide ores in the Fredericktown district. Nickel ores also occur in the Lancaster county, Pennsylvania; at the Key West Mine, Nevada; Piedmont region, Fauquier Co., Amherst Co., and Floyd Co., Virginia; in Jackson county, North Carolina; Riddles, South Oregon; in the Fremont county, Colorado; and near Wickenburg, Arizona. A. F. Buddington described the nickel ores of Alaska. In **Mexico**,[38] nickel-cobalt ores occur in Western Chihuahua; in the Toliman district, Queretaro; and the Esmeralds and Pilmano mines of Jalisco. In **Porto Rico**,[39] there is a deposit of nickeliferous ore west of Mayaguez. In **Cuba**,[40] there are nickeliferous ores in the districts of Mayari, San Felipe or Cubitas, and Moa on the north coast of the island. In **Santo Domingo**,[41] there is a low-grade nickel ore at the Perseverancia mine at Sierra Prieta.

South America.—In **Brazil**,[42] nickeliferous pyrrhotite occurs near Villa de Livramento, Minas Geraes. In **Chile**,[43] there is a deposit on the Pajonales, department of Copiapo, Atacama. In **Peru**,[44] there is a group of nickel and cobalt ore veins in the Vilcabamba district, Cuzco. In **Venezuela**,[45] there are deposits in Neuva Providencia.

Australasia.—In **Queensland**,[46] there are no deposits of economic value. In **New South Wales**,[47] small deposits of nickel have been reported from time to time. The one at Port Macquarie consists of a nickeliferous asbolite or earthy cobalt. In **Tasmania**,[48] small deposits of nickeliferous pyrrhotite occur in the North Dundas district near Zeehan. Veins of garnierite occur near Trial Bay on the west coast. Other small deposits have been reported. In **New Zealand**,[49] W. Skey, in 1885, reported an occurrence of a native nickel-iron alloy. It was described by G. H. F. Ulrich.

Reliable statistics[50] for the world's production of nickel are not available. Only in the case of Canada are official returns of the ores mined and treated available, but since Canada now produces 80 to 85 per cent. of the total, a close approximation can be estimated. The New Caledonian output was considerably reduced during the Great War owing to transport difficulties, etc. W. G. Rumbold compiled the following data up to 1920, for the world's production of nickel ore expressed in terms of the metal content in metric tons:

	Per cent. Nickel	1913	1914	1918	1919	1920
Canada . .	Metal	22,533	20,646	41,973	20,211	27,829
Germany .	2·00	271	251	1,871	583	—
Greece . .	0·50	87	68	60	5	—
Norway . .	1·03	690	794	33	200	422
Sweden . .	1·00	—	2	25	4	—
New Caledonia	5·6	5,219	5,272	874	87	181
United States .	45·0	2,651	2,379	1,771	1,716	2,028
	Metal	219	384	400	464	331
World's production .		31,670	29,796	47,007	23,270	30,791

Many European countries import ores and mattes from other countries from which refined nickel is obtained. According to the *Metallgesellschaft*, the world's production of refined nickel is:

	1896	1900	1905	1910
Germany	822	1,376	2,700	4,500
France	1,545	1,700	2,200	1,500
England	340	1,450	3,100	3,500
America	1,700	3,000	4,500	10,000
Other Countries . .	—	—	—	600
Total	4,407	7,526	12,500	20,100

The prices have not varied very much. The following represent average London prices per long ton :

1917	1918	1919	1920	1921	1922
£200	£210	£200	£226	£195	£158

Nickel appears as an accessory constituent of many minerals. J. H. L. Vogt,[51] and W. Schornstein discussed the occurrence of nickel in igneous and other rocks. W. N. Hartley and H. Ramage observed nickel in numerous iron ores ; and it has thus been reported in *aikinite* by M. H. Boye, W. Gregory, and R. Hermann ; in *abloclastite* by W. Gregory ; in *animikite* by H. Wurtz ; in *antimonial fahlerz* by A. Daubrée ; in *arsenopyrite* by D. Forbes, G. Tschermak, A. Frenzel, H. How, J. Rumpf, W. F. Hillebrand, A. Arzruni, and A. Guyard ; in *carrollite* by C. L. Faber, and J. L. Smith and G. J. Brush ; in *chathamite* by F. von Kobell ; in *cheleutite* by L. W. McCay ; in *copper ores* by H. Väyrynen ; in *chloanthite* by L. W. McCay, and G. Rose ; in *chromite* by E. Bechi ; in *chromopocotite* by T. Petersen ; in *clays* by L. Azema ; in *cobaltiferous manganese ore* by L. W. McCay, and G. la Valle ; in *copper pyrites* by H. Bowman, and S. G. T. Bryan ; in *danaite* and *glaucodote* by A. Breithaupt, D. Forbes, and G. C. Hoffmann ; in *domeykite* by A. Weisbach ; in *epiboulangerite* by M. Websky ; in *erythrite* by M. H. Boye, J. Lindaker, J. F. Vogl, T. Petersen, and G. la Valle ; in *fahlerz* by H. Peltzer, T. Petersen, F. Sandberger, and A. Hilger ; in *frigidite* by A. Funaro ; in *gabbro* by D. Forbes, C. F. Naumann, and O. Köttig ; in *gneiss* by A. W. Stelzner ; J. A. Smythe, *goslarite*, *epsornite*, and *melanterite ;* in *kämmererite* by J. B. Pearse ; in *köttigite* by M. H. Boye ; in *lavendulite* by E. Goldsmith ; in *linnæite* by T. Petersen ; in *lithiophorite* by A. Frenzel and C. Winkler, and A. Weisbach ; in *limonite* by F. Pisani ; in *magnetite* by T. Petersen ; in *marcasite* by B. Kosmann ; in *moresnetite* by H. Risse ; in *nephrite* by A. Kenngott ; in *olivine, chrysolite*, and *peridote* by F. A. Genth, R. Beck, R. Beck and R. Hermann, W. S. von Waltershausen, A. Erdmann, L. Ricciardi and S. Speciale, H. B. von Foullon, and W. Jung ; in *pennite* by R. Hermann ; in *picrolite* by B. Silliman ; in native *platinum* by S. P. de Rubies ; in *pyrites* by T. L. Walker, W. Gregory, M. H. Boye, K. T. Liebe, J. B. Mackintosh, C. W. Dickson, F. Sandberger, H. Hahn, A. Knop, E. S. Dana and B. J. Harrington, A. Hilger and L. Mutschler, A. Streng, K. Vrba, A. Funaro, and B. Neumann ; in *pyrolusite* by W. Gregory ; in *pyrrhotite* by J. H. L. Vogt ; in *schuchardtite* by A. Schrauf, and G. Starkl ; S. P. de Rubies in *chromite*, and in native *platinum ;* in *serpentine* by R. Hermann, J. L. Smith and G. J. Brush, T. S. Hunt, E. von Fellenberg, and A. Cossa ; in *pallasite* by P. N. Tschirvinsky ; in *stalactitic limestone* by B. Kosmann ; in *talc* by F. Stolba, T. Scheerer and R. Richter, F. A. Genth, M. F. Heddle, and I. A. Bachman ; in *tectites* by E. Preuss ; in bismuthiferous *tesserel pyrites* by W. Ramsay ; in *tetrahedrite* by W. Gregory ; in *uranochalcite* by R. Hermann ; in *wad* by C. P. Williams ; in *wattevillite* by S. Singer ; and in *wavellite* by A. Gages. W. Baker, O. L. Erdmann, and H. Weiske observed nickel in some samples of commercial *lead* and *iron*, and E. D. Campbell in American pig irons. S. P. de Rubies reported 0·1 per cent. of nickel in native platinum from Kitbim, Urals ; and the subject was discussed by A. Daubrée. J. Sebelien observed the presence of small proportions of nickel and cobalt in some ancient Egyptian and Mesopotamian bronzes ; R. A. Dart, and T. G. Trevor, 3 per cent. of nickel in an ancient bronze from the Transvaal.

Many basic igneous rocks contain small proportions of nickel. Thus :[52]

the trapp dyke that outcrops at the Rideau canal, Ontario, has 0·612 per cent. Ni ; the serpentines of Quebec contain small proportions—0·15 to 0·26 per cent. NiO ; and a peridotite (dunose) from British Columbia has 0·10 per cent. NiO. F. W. Clarke observed that the Massachusetts serpentines had 0·17 to 0·53 per cent. NiO ; Connecticut—hornblende norite, 0·9 per cent. ; New York—peridotite, 0·9 per cent. ; Pennsylvania—pyroxenite, 0·5 per cent. ; North Carolina—pyroxemite, 0·11 per cent. ; Kentucky—periodotite, 0·10 per cent. ; Missouri—granite, 0·20 per cent., and a porphyry, 0·15 per cent. ; Texas—nepheline basalt, 0·06 per cent. ; Michigan—peridotite, 0·21 per cent.,

and a diabase, 0·10 per cent.; Minnesota—hypersthene gabbro, 0·06 per cent., and an olivine gabbro, 0·16 per cent.; Yellowstone National Park—pyroxene-mica-diorite, 0·09 per cent., a quartz-pyroxene-mica diorite, 0·05 per cent., an allgite-andesite porphyry, 0·06 per cent., a monzonite, 0·10 per cent., a quartz-diorite porphyry, 0·19 per cent., a quartz-mica-diorite porphyry, 0·17 per cent., and a banakite dyke, 0·14 per cent.; Montana—hornblende picrite had 0·09 per cent., pyroxenite, 0·11 per cent., peridotite, 0·16 per cent., and shonkinite, 0·07 per cent.; Idaho—diorite, 0·12 per cent.; Colorado—perovskite—magnetite rock, 0·05 per cent.; Arizona—mica basalt, 0·08 per cent.; Nevada—andesitic perlite, 0·07 per cent.; California—quartz diorite, 0·05 per cent., altered peridotite, 0·09 per cent., diorite, 0·05 per cent., gabbro, 0·06 per cent., and pyroxenite, 0·11 per cent.; Oregon—peridotite, 0·10 per cent., olivine, 0·26 per cent., hypersthene—augite andesite, 0·05 per cent., and serpentine, 0·13 per cent.; and Hawaiian Islands—picritic basalt, 0·09 per cent., plagioclase basalt, 0·05 per cent., porphyritic gabbro, 0·12 per cent., olivine basalt, 0·08 per cent., and olivine, 0·34 per cent. The subject was discussed by T. G. Bonney, and C. S. Ross and E. V. Shannon.

M. Mazade,[53] O. Henry, and H. J. Homberg observed nickel in the **mineral water** of Nérac, and Ronneby; and S. S. Miholic studied the subject. A. Martini observed the presence of traces of nickel in many plants. W. Vernadsky discussed the subject. J. S. McHargue also observed the occurrence of traces of nickel and cobalt in soils, plants, and animals. Nickel also occurs in **coals** and in **peats**; V. M. Goldschmidt and C. Peters found it in coals; and, according to E. de Golyer, it occurs in petroleum. G. Bertrand and M. Mokragnatz found very small proportions of nickel and cobalt occurring in most plants—*vide* the occurrence of cobalt. J. A. Buchner and C. G. Kaiser found nickel to be present in the ash of some gum benzoin; K. Kraut, and A. Braun, in the ash of peats and coals; and G. Tissandier, in some samples of atm. dust. A. Martini observed that nickel is a normal constituent of bones; and H. M. Fox and H. Ramage found nickel in some animal tissues. The foot of the *Haliotis*, for instance, had 0·004 per cent. of nickel but no cobalt. Usually the nickel is accompanied by a small proportion of cobalt.

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§ 3. The Extraction of Nickel

Nickel was extracted on a commercial scale at Schneeberg, Saxony, and the chief ores were the arsenical minerals associated with the cobalt deposits of Saxony and Bohemia. In 1838, a plant for working the Swedish pyrrhotic ores was erected, and soon afterwards Norway began producing the metal from similar ores carrying 1·4 to 1·7 per cent. of nickel, and Norway became the main source of the world's supply. In 1877, the Norwegian ores were superseded by the garnieritic ores from New Caledonia; in 1886, Canada became a competitor with pyrrhotic ores, and, since 1905, she has been the main producer for the world's market.

The methods of extracting nickel vary according to the type of ore employed—sulphide, arsenide, or hydrosilicate. The ores furnish nickel, and in the two former cases, copper. In addition there are in some cases the by-products cobalt, gold, silver, and the platinum metals to be recovered. Some ores contain mercury.

The Sudbury ores are hard and compact so that the ore is mined without special difficulty, and mainly by underground workings. The ore is crushed and that portion which passes 1-inch trommel holes is known as *fine*. This amounts to about 30 per cent. of the ore mined. The ore is then carried on picking belts, where the so-called *rock* is picked out by hand. The rock thus discarded amounts to about 19 per cent. of the material hoisted from the mines. The discarded rock carries about 0·62 per cent. of nickel, and about 0·60 per cent. of copper, while the *ore* carries 3·58 per cent. of nickel and 1·58 per cent. of copper. The richer ore is directly smelted, whilst the lower grade ore has to be concentrated before smelting. The New Caledonia ore is friable and the depth of the workable ore is restricted to depths of 25 to 30 feet so that they are obtained from open pits. The ore is picked or barred down, and then sorted. The payable portion is gathered into heaps and then transported for shipment, or other treatment, and the waste is trammed to a dump. Flotation methods of concentration are not in general use at Sudbury, or New Caledonia. Magnetic concentration has been tried by C. E. Hugoniot,[1] and G. C. Mackenzie; oil flotation was tried by H. E. T. Haultain, but the results were not successful.

Quite a number of papers [2] have been written on the extraction of nickel; and there are also a number of special works devoted to the subject:

L. Ouvrard, *Industries du chrom, du manganese, du nickel, et du cobalt*, Paris, 1910; H. L. Herrenschmidt and E. Capelle, *Le cobalt et le nickel*, Rouen, 1888; H. Copaux,

Recherches expérimentales sur la cobalt et le nickel, Paris, 1905 ; J. Meunier, *Cobalt et nickel*, Paris, 1889 ; A. M. Villon, *Cobalt et nickel*, Paris, 1891 ; W. Borchers, *Metallhüttenbetriebe —Nickel*, Halle a. S., 1917 ; H. Moissan and L. Ouvrard, *Le nickel*, Paris, 1896 ; *Report of the Royal Ontario Nickel Commission*, Toronto, 1917 ; A. P. Coleman, *The Nickel Industry*, Ottawa, 1913 ; P. D. Merica, *Trans. Canada Inst. Min. Met.*, **29**. 1, 1926 ; W. H. Baldwin, *Journ. Chem. Educ.*, **8**. 2325, 1931 ; A. J. Wadhams, *Metals Alloys*, **2**. 165, 1931 ; W. P. Blake, *Chem. News*, **48**. 87, 1883 ; G. G. Urasoff and M. L. Tschernomorsky, *The Metallurgy of Nickel*, Moscow, 1931.

The general procedure in dealing with the sulphide ores involves, (i) Roasting of the ore. Pyritic smelting as employed for copper ores does not necessitate roasting ; the process for nickel was tried by E. H. Robie.[3] (ii) Smelting the roasted ore for a regulus or crude matte. (iii) Enriching the crude matte ; and (iv) Converting the enriched matte into crude metal.

The roasting of the sulphide ore.—The Sudbury ore is first roasted to remove part of the sulphur. The roasting may be conducted in heaps when the agricultural work in the surrounding country is of so little value that there is no risk of compensating damages for the injury to vegetation by the escaping noxious sulphurous fumes. In Norway one plant had to abandon heap roasting, and even smelting could not be conducted in the summer months on account of injury to neighbouring forests. In heap roasting, the ore, crushed to a convenient size, is piled on a bed of brushwood, 5 to 15 feet high, so as to allow a circulation of air. One pile may contain a few thousand tons, and after the brushwood has started the combustion, the heap may burn from six to twenty weeks. Roasting in reverberatory furnaces is more costly, and the same remark applies to special roasting furnaces. In exceptional cases there may be a market for products like sulphite liquor, and sulphuric acid, which can be manufactured from the flue gases up the roasting furnaces. The roasting is not allowed to oxidize fully the ore ; enough sulphur is allowed to remain so that it can combine with the nickel, copper, and some of the iron in the first smelting to form a crude sulphide matte.

The smelting of the ore for a crude matte.—The partially roasted ore is smelted with the correct proportions of coke and siliceous fluxes in blast-furnaces so as to yield a matte of iron, copper, and nickel sulphides. In some cases, the roasted ore is self-fluxing. In the smelting the pyrrhotite in these ores is almost entirely converted into iron silicate in the smelting furnace. The ferric oxide present is reduced in the furnace by the sulphur of the pyrites to form ferrous oxide, which, in the presence of silica, forms a slag : $FeS+3Fe_2O_3+nSiO_2=SO_2+7FeO.nSiO_2$. Any nickel monoxide which may be present reacts with an equivalent amount of ferrous sulphide to form nickel sulphide and ferrous oxide, which in turn passes into slag. The slag is somewhere between a monosilicate and a disilicate, although in some cases it approaches a subsilicate. The slags from two different plants contained :

		SiO_2	Al_2O_3	FeO	CaO	MgO
Blast-furnace slag	I	38·56	7·61	35·64	13·55	4·79 per cent.
	II	38·0	10·0	43·0	4·5	2·5 ,,

The copper and nickel in the slag range up to about 0·4 per cent. The slags may be rejected, or part may be used again in similar smeltings, or in later stages of the concentration process. The matte must contain sufficient iron to prevent nickel passing into the slag. The crude matte from two different furnaces contained approximately :

		Copper	Nickel	Cobalt	Iron	Sulphur
Crude matte	I	22·5	20·5	—	30·0	— per cent.
	II	13·2	17·8	0·45	42·0	21·4 ,,

The precious metals in the ore accumulate in the matte, and in the latter case, there were present 1·90 ozs. of silver, 0·35 oz. of platinum, and 0·35 oz. of palladium per ton. According to G. P. Schweder, the sulphur in the matte is present as monosulphides of silver, copper (ous), nickel, and iron ; and if insufficient sulphur is

present to form NiS, and FeS, the excess of metal dissolves in the molten sulphide. Any nickel silicate which may be formed is decomposed by the iron sulphide to form iron silicate and nickel silicate, and so long as enough iron sulphide is present, only a very small proportion of nickel can pass into the slag—prills of matte may be imprisoned in the slag if its viscosity in the furnace is too great. If the ores have been over-roasted nickel will appear in the slag, and in that case some unroasted ore is mixed with the furnace charge. Copper silicate behaves like nickel silicate, but the cobalt silicate does not react so easily with the iron sulphide, and when cobalt silicate is produced, it will pass into the slag. Any antimonates or arsenates are reduced and volatilized in the furnace; if only small proportions of arsenic and antimony are present, they pass into the matte. Gypsum in the ore is reduced to sulphide, and it acts like iron sulphide on iron and copper oxides. V. Tafel and F. Klewata discussed the reaction.

The enriching of the crude matte.—In former times, in some localities, the crude mattes had so low a proportion of copper and nickel that the matte was subjected to a preliminary concentration before being refined. This was done by roasting the crude matte in heaps, stalls, shaft furnaces, reverberatory furnaces, or muffles, and again smelting it with a suitable flux—quartz, glass, or slag—in shaft or reverberatory furnaces. This treatment removes a relatively large proportion of iron from the matte. The subject was discussed by E. F. Kern and H. W. Walter, and H. W. Walter. C. Schnabel thus described the chemical changes involved in the smelting of the roasted matte:

Ferric oxide is reduced to ferrous oxide by the undecomposed sulphide of iron present; this passes into the slag, and sulphur dioxide is formed; a further quantity of sulphide of iron is changed to ferrous oxide by the nickel and copper oxides, and also slagged, the oxides of these metals meanwhile becoming sulphides; further copper oxide and undecomposed copper sulphide give metallic copper and sulphur dioxide. This copper is reconverted into sulphide at the expense of some iron sulphide. The iron thus separated is partly taken up by the matte, partly acts upon a corresponding amount of ferric oxide, giving more ferrous oxide to be slagged. There is no action between nickel oxide and sulphide. The various metallic sulphides unite to form the concentrated matte.

D. H. Browne made observations on this subject. Under modern conditions this preliminary concentration of the crude matte is unnecessary, and they can be refined directly; but, in any case, the coarse matte can be concentrated or refined by an oxidizing roasting followed by a reducing smelting as just indicated for the treatment of poor mattes, or the crude matte is enriched as in the case of copper by melting it in a cupola and running it into a ladle whence it is charged into a bessemer converter, or the molten matte may be run into ladles directly from the blast-furnace, and thence on to the converter. The converter is made like those used in purifying copper, and they have a quartz lining. During the blow, which may occupy 25 to 90 minutes dependent on the proportion of iron, quartz sand is added to slag the iron, and to prevent undue corrosion of the lining. When the proportion of iron has been reduced to about 0·5 per cent., the blast is stopped, and the matte is poured. The refining of the matte by a blast of iron was suggested by T. Gibb and C. Gelstharp in 1870. Attempts to carry the refining process further have not been successful because up to a certain stage the nickel is more easily oxidized than sulphur, and because the heat liberated by the oxidation of the sulphur is not sufficient to keep the matte in a fluid condition. The slag from one converter contained approximately:

	FeO	SiO_2	Cu	Ni	S
Converter slag	67·0	28·0	1·0	1·7	0·5 per cent.

the copper and nickel are present partly as silicates, and partly as a mechanical mixture. The slag is returned to the ore smelting blast-furnace. The refined matte from two different plants contained:

	Ni	Cu	Fe	S	SiO_2
Refined matte I	37·78	41·40	0·65	18·37	0·19 per cent.
Refined matte II	39·96	43·36	0·30	13·76	— ,,

The proportion of sulphur is much less than is needed to form sulphides with the metals present. The copper is probably present as cuprous sulphide, and the nickel and iron partly as sulphides and partly as solutions of the metals in the mixed sulphides. The refining process at Port Colborne was described by R. L. Peek, and there are several modifications—*e.g.*, by J. Savelsberg.

The conversion of the refined matte into crude nickel.—The so-called *Orford process* for separating copper and the nickel, devised by J. L. Thomson, R. M. Thompson, and C. C. Bartlett, in 1893, is practised at the Orford Company's Works, at Constable Hook, New Jersey. The process was described by V. von Ehrenwerth. The process depends on the fact that copper sulphide combines with an alkali sulphide, forming a fusible double sulphide, whilst nickel sulphide does not do so; consequently, if a mixture of copper and nickel sulphides be fused with an alkali sulphide and allowed to cool, it will separate into two layers, with most of the copper above, and most of the nickel below. The two products are tapped separately from the melting-furnace. The charge is a mixture of sodium sulphate and coke which forms alkali sulphide in the furnace. By repeating the process on the bottom layer, a mixture of iron and nickel sulphides is produced. The top layers of both operations are allowed to weather and are then fused with more matte, the bottom layer is returned to be treated with the second fusion with alkali sulphide, while the top layer is leached with water to recover the alkali sulphide by evaporating the soln. to dryness. The insoluble sulphide is then treated for copper. The nickel sulphide still contains iron. It is roasted to remove some of the sulphur, and then melted. This furnishes nickel sulphide freed from iron sulphide and a slag of ferrous silicate mixed with some nickel, and it is rejected. The nickel sulphide is roasted, and a little nitre is added to complete the oxidation, and a little common salt to convert any copper into the chloride. The roasted oxide is washed with water, and it is then ready for reduction to metal. Any platinum metals in the matte are also converted into chlorides during the chloridizing roast, and they pass into soln. during the leaching process. The nickel oxide can be reduced as indicated below. Two samples of nickel oxide obtained from Canadian matte had the compositions:

	(Ni,Co)O	CuO	Fe_2O_3	As	S	SiO_2	
Nickel oxide I .	97·5	0·4	1·5	0·3	0·03	0·3	per cent.
Nickel oxide II .	98·74	0·30	0·70	0·04	0·02	0·20	„

The so-called *Mond process,* devised by L. Mond and C. Langer, in 1889, depends on the formation and decomposition of volatile nickel and iron carbonyls under conditions where copper does not form a gaseous carbonyl. The bessemerized matte is crushed and roasted, in the *roaster,* to produce it as free as possible from sulphur. The crushed and screened product is treated with dil. sulphuric acid which removes about two-thirds of the copper oxide and about 1 per cent. of nickel oxide. The residue contains 45 to 60 per cent. of nickel oxide. The soln. is evaporated and the copper sulphate crystallized out; the iron and nickel sulphates accumulate in the mother-liquor, which is then evaporated to dryness, heated to decompose the sulphate, and the oxides introduced into the main process. The washed and dried residue, containing copper, nickel, and iron oxides, is treated with water-gas, in the so-called *reducer,* at a temp. below 300°; this reduces the nickel and copper oxides, but not the iron oxide. The product at 50° is then treated with carbon monoxide—obtained by passing the gas from the reducer over red-hot coke. The gas containing nickel carbonyl is then passed through a filter and into a chamber, the *decomposer,* at about 200°, when the nickel carbonyl is decomposed with the separation of nickel; the regenerated carbon monoxide returns to the volatilizer. The decomposer is a tower containing nickel shot. A layer of nickel forms on the shot. To prevent the granules adhering, they are kept in motion by the constant withdrawal of some of them from the bottom of the decomposing tower by means of a worm conveyor. The granules are passed over a screen. The larger shot are removed, and the smaller ores return to the top of the tower to receive another

deposit of nickel. The shot being alternately exposed to and withdrawn from the action of this gas, a series of concentric rings of nickel are deposited about the original nucleus. When a Mond-nickel shot is hammered on an anvil, the various coatings will be broken open, and its structure revealed. The residue in the volatilizer still contains some nickel; and it is returned to the reducer. When most of the nickel has been extracted the residue is returned to the roaster. The process was described by A. P. Coleman, W. C. Roberts-Austen, and G. B. Shipley. Two specimens of nickel obtained by the Mond process had the composition:

	Ni	Fe	S	C	Insoluble	
Nickel I	99·82	0·10	0·0068	0·07	—	per cent.
Nickel II	99·43	0·43	0·0099	0·087	0·026	,,

Other methods have been suggested for treating the refined copper-nickel matte. V. von Ehrenwerth described a method for removing copper from nickel mattes by blowing in a converter with a lining of a basic material or coke. The iron is first slagged off, then the nickel, and the copper separates out lastly as metal. The process has not been successful. S. H. Emmens proposed a chloridizing roasting of the matte in the presence of steam; extracting the chlorides of copper and other metals with water; and smelting the residue of nickel and iron oxides with sodium sulphide, and charcoal. The nickel matte is roasted, and the resulting nickel oxide reduced to metal. N. V. Hybinette and A. R. Ledoux proposed to separate nickel from its molten matte by adding manganese dioxide, because, under these conditions, manganese and copper combine more readily with sulphur than is the case with nickel. The nickel and its sulphide settle to the bottom, and the layer of sulphides of copper and manganese float on top. The upper layer is removed and the residue again treated with manganese. This completes the isolation of the nickel. The top layers are used for the extraction of copper and manganese.

If the enriched matte be roasted, and the resulting oxide reduced by carbon, an alloy of nickel and copper is formed which may be used for making German silver, or other alloys. The process was described by D. Levat, C. A. M. Balling, C. Schnabel, and G. P. Schweder. Analyses of the nickeliferous copper—*Garkupfer*—were reported by C. Schnabel, F. A. Genth, G. W. Wille, F. Heusler, G. P. Schweder, C. A. M. Balling, G. Hamprecht and L. Schlecht, and V. Tafel and F. Kleweta. The compositions of a refined matte and the resulting alloy were:

	Ni	Cu	Fe	S	As,Sb	
Refined matte	32·59	52·00	0·41	17·71	0·11	per cent.
Alloy	39·95	59·5	0·64	—	—	,,

The extraction of nickel from arsenical ores—e.g., niccolite or kupfernickel, chloanthite, and nickel glance. Arsenical ores are now very little worked. The ores, freed from gangue, were first roasted to remove some of the arsenic. The iron can be nearly all oxidized and slagged before the nickel arsenide is attacked. This furnishes a *crude speiss*. The crude speiss is again roasted and enriched by a second fusion to furnish an *enriched speiss*. The operations are here analogous to those employed in the preparation of the coarse and enriched mattes in working with sulphide ores, only now, in the roasting, stable arsenates are formed. The roasted charge is therefore mixed with carbon strongly heated so as to reduce the arsenate to arsenide. The arsenic can also be removed by heating the nickel arsenide with nitre and soda whereby the nickel furnishes nickel oxide, and the arsenic a soluble arsenate which can be removed by leaching with water. The arsenic can also be removed as volatile chloride by the chloridizing roast with common salt. The nickel oxide can then be reduced in the usual manner.

The extraction of nickel from garnierite.—Many analyses of the New Caledonian ore—garnierite—have been reported. The composition is usually taken to lie between the following limits:

	NiO	SiO_2	Fe_2O_3	Al_2O_3	MgO	H_2O	
Garnierite	9 to 17	41 to 46	5 to 14	1 to 7	6 to 9	8 to 16	per cent.

For a time, the ore was reduced with suitable fluxes—fluorspar, cryolite, soda, manganese ore—and powdered coal or coke, in a blast-furnace, and the resulting ferro-nickel obtained approximated :

	Ni	Fe	Si	S	C
Ferro-nickel .	68·20	27·82	1·62	1·02	2·50 per cent.

The process was not satisfactory. It was found better to smelt the ore in a blast-furnace with sulphur so as to form a regulus or matte. The sulphur was added in the form of alkali waste (calcium sulphite), or as gypsum, or iron pyrites. Suitable fluxes are added to form a slag. The mixture is briquetted and smelted. The resulting regulus or matte contains up to 50 per cent. of nickel. The regulus is then enriched either by roasting and melting, or in a converter as in the case of the mattes from the sulphide ores. The enriched matte is then roasted for oxide and reduced. The ore contains no copper, so that the resulting nickel oxide can be directly reduced to nickel. The extraction of nickel from garnierite in Brazil was discussed by E. de Oliviera, J. L. Fohlen, A. Guerreiro, M. Ballay, E. Reitler, and H. E. de Aranjo ; and from silicate ores, by B. Bogitch, T. Tatebe, and J. Hissink.

The extraction of nickel from metallurgical products.—Copper ores may contain nickel which collects in the *blister copper* if but little arsenic is present in the ore. The nickel is obtained by subjecting the copper to a blast which gives a dross containing nickel (and cobalt), and copper with a reduced proportion of nickel. The dross, when smelted in a blast-furnace, yields a copper-nickel alloy. The treatment—blowing and smelting—of the copper-nickel alloys so obtained can be repeated until finally an alloy with the desired proportion of nickel is obtained. The dross can also be smelted with pyrites to form a nickel matte ; or with barytes and arsenical pyrites to form a speiss and a copper matte ; or it can be treated by a wet process. C. H. Fulton gave the following for the by-products obtained from 100 tons of blister copper :

	Gold (ozs.)	Silver (ozs.)	Platinum (ozs.)	Palladium (ozs.)	Nickel (lbs.)
Garfield, Utah . .	288	3,480	0·342	1·183	40
Steptoe, Nevada . .	169	550	1·016	4·402	60
Omaha, Nebraska .	36	23,090	1·825	6·486	944
Mountain, California .	1,418	10,990	1·320	0·607	11·5
Tacoma, Washington .	2,187	8,710	0·710	3·327	770
Aguascalientes . .	482	67,300	0·416	0·226	12
Cerro de Pasco . .	170	9,900	0·319	0·589	32
Mount Lyell . .	464·5	7,205	0·624	1·374	166

Nickeliferous *speiss* obtained as a by-product in the treatment of some copper, lead, and silver ores contains nickel, and it can be worked up by a modification of the process used for extracting nickel from arsenical ores. In the refining of dross copper, and in the treatment of nickel ores, *slags* may be obtained which contain nickel. The slags may be smelted in a blast-furnace with pyrites or arsenical pyrites to form a matte or speiss, and treated as indicated before. The speiss may be treated for cobalt. The nickel present in *iron sows* may be recovered as a nickel copper alloy by treatment in a small refining hearth. The iron oxide formed by the blast is slagged with quartz. J. L. Fohlen obtained nickel matte by passing the gases from the destructive distillation of lignite over a mixture of garnierite and calcium sulphide, and recovered the hydrocarbons of low b.p. formed as a by-product.

Wet processes for the extraction of nickel from its ores.—Wet processes are used in some cases to extract nickel from speiss and matte containing nickel, cobalt, and copper ; but whilst several methods have been suggested for extracting nickel directly from its ores, none seems to have been established as an economic success. It is cheaper to concentrate the nickel to a speiss or matte in the dry way, and particularly so with sulphide and arsenide ores. When a sulphide or arsenide ore

is to be treated by a wet process, it is roasted before being submitted to the action of solvents. H. C. Mabee and A. E. Smaill[4] proposed to smelt the nickeliferous pyrrhotitic ore with an alkali flux under non-oxidizing conditions to obtain a low-grade matte containing all the copper, nickel, and precious metals. This matte, on exposure to the air, disintegrates into a fine powder, which is roasted in a two-stage mechanically-rabbled furnace, in the first stage of which the temperature is maintained at 400° and in the second stage at 600°. The product is mixed with 10 per cent. of its weight of sodium chloride, damped with water, and again roasted at 400°, the issuing vapours being absorbed in water. This water is then used to leach the roasted product, and leaching is continued with 10 per cent. sulphuric acid. The residue contains practically all the iron and the greater part of the nickel, but only a small proportion of copper and sulphur, and is amenable to direct smelting for the production of nickel steel. The leach liquor is electrolysed for the recovery of copper, then treated for the removal of iron, and again electrolysed to recover the nickel. Over 90 per cent. of the copper and 40 per cent. of the nickel are said to be obtained as pure metals.

S. H. Emmens suggested dissolving the nickel from pyrrhotite ores by the solvent action of a soln. of ferric sulphate, but the solvent action is more rapid with the roasted ore. Nickel is precipitated from the soln. as hydrate. In the most favourable cases it was found that only one-third the amount of nickel and two-thirds the amount of copper in the ore are dissolved by the soln. of ferric sulphate. H. L. Herrenschmidt heated the ore with a soln. of ferric chloride, and precipitated cobalt and nickel from the soln. by manganese sulphide or hydroxide. C. W. B. Natusch, and W. Schöneis extracted the roasted ore with a soln. of ferric chloride, evaporated the soln. to dryness, and heated it until the iron chloride was decomposed. On extracting the soln. with water, nickel, cobalt, copper, gold, silver, and zinc chlorides pass into soln. T. Macfarlane subjected the partially roasted ore to a chloridizing roast with common salt, at a low red-heat; and to the extract in hot water added a little sodium hydroxide to precipitate any iron, sodium sulphide to precipitate any copper, and the sodium hydroxide to precipitate the nickel as hydroxide. A. Drouin digested the ore, roasted at a low temp., with an acidified 20 to 25 per cent. soln. of sodium chloride. The lead was precipitated as chloride by cooling the soln., the copper was precipitated by iron, the iron by calcium carbonate, and the nickel by lime-water. P. de P. Ricketts dissolved the nickel and copper with dil. sulphuric acid, and precipitated the nickel as a basic sulphate by alkalies and alkali sulphates. The basic sulphate is converted into oxide by calcination, and the copper is precipitated from the soln. electrolytically. C. G. Richardson dissolved the copper and nickel in hydrochloric acid, and separated the two salts by fractional distillation in hydrochloric acid. H. Grosse-Bohle precipitated the cobalt and nickel from their hot soln. in hydrochloric or sulphuric acid by means of zinc. The copper was first precipitated from the soln. by iron. C. Perron digested the ore in an ammoniacal soln. of ammonium sulphide, and precipitated the nickel from the soln. in the usual manner. The Metals Extraction Corporation extracted the nickel by means of a soln. of magnesium chloride at 250°. D. Lance found that when the soln. in a soln. of ammonia or an amine is heated, the metals are precipitated in the order: Zinc, cadmium, cobalt, nickel, copper, and silver. G. Schreiber treated the soln. with calcium carbonate to precipitate iron, aluminium, and arsenic; with hydrogen sulphide to precipitate copper; with soln. of alkalies or alkaline earths, say milk of lime, to precipitate cobalt and nickel, and lastly manganese. A. Seigle digested the ore with hydrochloric acid, chlorine water, and potassium cyanide. E. Günther and R. Franke devised a process for extracting nickel from the anode slimes obtained in the refining of copper. E. R. Thews discussed the re-melting and refining of scrap nickel.

Many wet methods have been proposed for extracting the nickel from ores of the type of garnierite, rewdanskite, etc. Methods were described by E. André,[5] A. Badoureau, F. R. Bode, B. Bogitch, A. Cahen, J. J. Hissink, F. O. Kichline, H. C. Mabee and A. E. Smaill, W. A. Dixon, R. Lake, and H. Parkes.

R. Hermann dissolved rewdanskite in sulphuric acid, and evaporated the soln. until acid began to vaporize; the mass was then lixiviated with water, the iron in the soln. oxidized with salt and nitre, and then precipitated by calcium carbonate. The nickel was precipitated by sodium sulphide. J. P. Laroche and J. P. Pratt treated garnierite with sulphuric acid; added to the soln. an amount of ammonium sulphate equivalent to the proportion of nickel present to precipitate ammonium nickel sulphate; and added sodium carbonate to the soln. of ammonium nickel sulphate in boiling water to precipitate nickel carbonate. In place of ammonium sulphate, an alkali oxalate can be added to precipitate nickel oxalate, and the oxalate furnishes nickel carbonate when

boiled with a soln. of sodium carbonate. G. Rousseau treated the hydrochloric acid soln. with bleaching powder to oxidize the iron, and precipitated the iron with calcium carbonate; then precipitated the nickel with milk of magnesia. I. Kamiensky oxidized the iron in a hydrochloric acid soln. by chlorine, and precipitated it with magnesium carbonate; nickel was precipitated from the decanted soln. by sodium carbonate. M. Araud heated in retorts a paste made of the ore with hydrochloric acid so as to volatilize the chlorides which were condensed in water. The iron was precipitated from the soln. by calcium carbonate, and the nickel by milk of lime. M. Sebillot crystallized ammonium nickel sulphate from a sulphuric acid soln. of the ore to which ammonium sulphate had been added. In a second process, the ore was heated with sulphuric acid in a reverberatory furnace; the solid mass was leached with water; iron was precipitated from the soln. by calcium carbonate after oxidation with bleaching powder; magnesium was precipitated by sodium phosphate; and nickel sulphate was crystallized from the mother-liquor. G. G. Urazoff and M. M. Romanoff treated the washed ore with sulphur dioxide or sulphurous acid as solvent, and obtained good yields with ore having 0·9 to 5·08 per cent. of nickel. A. H. Allen treated the ore with a mixture of sulphuric acid and sodium nitrate; heated the mass to redness; lixiviated with water; precipitated from the soln. the chromium and iron by calcined magnesia, and the nickel by hydrogen sulphide. P. Christofle suggested several processes. (i) The hydrochloric acid soln. of the ore was treated with calcium carbonate or hydroxide to precipitate iron, and with milk of lime to precipitate the nickel; (ii) the ore was heated with a conc. soln. of oxalic acid, the nickel remained undissolved, and the residue reduced for nickel; (iii) a hot, conc. hydrochloric acid soln. of the ore when cold was treated with bleaching powder, and nickel oxalate precipitated by oxalic acid; or the iron and aluminium were precipitated by calcium carbonate, and the nickel by lime water and bleaching powder. H. L. Herrenschmidt treated the ore with a soln. of ferrous sulphate to dissolve manganese, cobalt, and nickel as sulphates whilst ferric oxide remains as a residue. The addition of sodium sulphides precipitates cobalt and nickel as sulphides, and any manganese sulphide in the residue is removed by treatment with a soln. of ferric chloride. The manganese is recovered as calcium manganite. The mixed sulphides of cobalt and nickel are roasted to sulphates, and the cobalt and nickel are separated from the soln. of the sulphates in hot water. In another process, H. L. Herrenschmidt precipitated the iron from the soln. by copper carbonate, and the copper by nickel hydroxide or carbonate, and the remaining soln. of nickel and cobalt sulphate was treated for cobalt and nickel. T. Storer digested the garnierite with a soln. of ferric chloride at 187° in an autoclave; the nickel passes into soln. as chloride, whilst the iron is left as oxide.

Wet methods have been suggested for the treatment of the nickel copper mattes. The matte is soluble in acids. With unroasted mattes, some copper sulphide contaminated with cobalt and nickel remains as a residue whilst the iron and most of nickel and cobalt pass into soln. The residue thus requires another special treatment for these two metals. It is therefore preferable to roast the matte before it is treated with acids—sulphuric or hydrochloric acid. With a successful roasting very little iron dissolves in either acid. Any arsenic present remains in the residue as ferric or copper arsenate. The treatment of the matte was described by C. Schnabel, H. Lundberg, A. Badoureau, L. Knab, and J. de Coppet; of speiss, by C. Schnabel, A. Badoureau, W. A. Dixon, and J. A. Phillips; and of slags, by C. Schnabel, M. Herter, and H. H. Vivian. T. Tatebe reduced the garnierite ore with carbon monoxide and hydrogen at 800° to 850°, and leached the product concurrently with aq. ammonia and a soln. of ammonium carbonate in air or oxygen. The nickel dissolved as $NiCO_3(NH_3)_n$. Calcination of the solid furnishes ammonia, carbon dioxide, and nickel oxide.

The older chemists obtained their nickel from copper-nickel-cobalt speiss which was usually "opened up" by roasting it at a gentle heat to prevent caking, and to volatilize the greater portion of the arsenic. Since some of the arsenic formed a nickel arsenate during the roasting, it was found advisable to mix the roasted ore with charcoal and roast the mixture. The operation was repeated as long as the vapour of arsenic was evolved. O. L. Erdmann[6] recommended keeping the roasted speiss moist in a cellar until it is hydrated, when it is more quickly attacked by the acid. A. Laugier, R. Tupputi, H. W. F. Wackenroder, P. Berthier, E. F. Anthon, J. Berzelius, and O. L. Erdmann dissolved the roasted speiss in nitric acid, or in aqua regia; J. Berzelius, O. L. Erdmann, and S. Cloez dissolved the roasted speiss in hydrochloric acid; A. Patera, O. L. Erdmann, R. Hermann, J. L. Proust, and T. Thomson used sulphuric acid. J. von Liebig heated the roasted speiss with 1 part of fluorspar and 3·5 parts of sulphuric acid above 100°; F. Wöhler fused the unroasted speiss with 3 parts of potassium carbonate and 3 parts of sulphur, and extracted the product with water. S. F. Hermstädt fused the speiss with 3 parts of

nitre; P. Berthier used 1 part of speiss with 1·5 parts of nitre and 2 parts of potassium carbonate; and R. Wagner, 5 per cent. of sodium nitrate and 10 per cent. of anhydrous sodium carbonate. C. R. Hayward described a process involving an oxidation roasting followed by leaching, etc.; A. B. Baghdasarain, and F. L. Duffield, a process involving a chloridizing roast of the sulphides, or oxides; P. Louyet described a process in use at a works in Birmingham in which the material was fused with chalk and calcium fluoride, and the resulting regulus roasted and taken up with hydrochloric acid. L. Thompson also used a somewhat similar process, and he dissolved the regulus in sulphuric acid. P. Berthier opened up the unroasted speiss by fusing it with 2 parts of lead oxide, and dissolving the product in nitric acid or in aqua regia. M. I. Gutman and A. D. Mayantz studied the precipitation of nickel hydroxide by magnesia or magnesium carbonate.

Electrolytic processes for the extraction of nickel.—The electrolytic extraction of nickel from its ores has not been successful: firstly, because the ores are too impure, and contain too little metal to be used as anodes or to be dissolved in any other way within the circuit; and secondly, because the preparation of nickel soln. from ores outside the circuit is difficult and expensive. The electrolytic method, however, can be used for nickel-copper mattes, and it has been profitably used in the separation of nickel-copper alloy since the operation is difficult when conducted by a dry process. In separating nickel from its mattes or alloys, the copper is deposited from an acidified electrolyte on the cathode whilst the nickel passes into soln. The soln. is then freed from other metals, and the nickel is deposited from its soln. by insoluble anodes.

The decomposition potential of nickel is greater than that of copper and many other metals. According to M. le Blanc,[7] for instance, the decomposition voltage of nickel sulphate is 2·09 volts, and of nickel chloride, 1·85 volts. Nickel is more electropositive than hydrogen, and the overvoltage on nickel is not great, and accordingly nickel is deposited from feebly acidic soln. This subject was discussed by F. Förster, who showed that in order to get thick deposits of nickel, the electrolyte must be hot, say, 60° to 70°, and the strength of the current, between 3·5 and 8·5 ampères per sq. ft. at 3 to 6 volts according to the nature of the electrolyte. W. Borchers found with insoluble anodes, using salts of cresolsulphonic acid, 5·5 ampères per sq. ft., and 2 to 2·5 volts were necessary; and K. Brand, using a soln. of the sulphate sat. with ammonia, and a carbon or iron anode, found 2·8 ampères per sq. ft., and 2·4 volts were necessary. According to C. Schnabel, a current of 914·9 ampères is needed to separate a kilogram of nickel per hour; and the energy for this is $24 \times 914{\cdot}9$ watts, or 2·99 H.P.; or allowing for a 12 per cent. loss in converting mechanical into electric energy, and a 25 per cent. loss in the current through conversion into heat, etc., 4·48 H.P., or about 9 kgrms. of coal, are needed for the deposition of a kilogram of nickel per hour.

E. Wohlwill investigated the separation of copper and nickel using an alloy as the anode, and a soln. of nickel and copper sulphates as electrolyte. The separation depends on the soln. of both metals and the precipitation of copper at the anode only at a particular voltage and current density. More copper is deposited at one electrode than is dissolved at the other, for the copper deposited at the cathode is equivalent to the copper and nickel dissolved at the anode; consequently, during the deposition of the copper, the decrease in the conc. of the copper and the increase in the conc. of the nickel proceed rapidly, so that very soon hydrogen is liberated at the cathode. An amount of copper, as sulphate, equivalent to the amount of nickel dissolved at the anode must be added to the electrolyte at intervals. When about $12\frac{1}{2}$ lbs. of nickel sulphate per cubic foot has accumulated in the electrolyte, the electrolysis is stopped; insoluble anodes are substituted for the nickel-copper anodes. Lead anodes are used when there is no risk of the formation of lead peroxide as is the case when ferrous sulphate is present. When most of the nickel has been removed from the electrolyte, the mother-liquor is evaporated and crystallized for the metal sulphates. W. Borchers studied the treatment of an alloy of nickel, copper, and iron (2 : 1 : 1) used as anode with an acid soln. of copper sulphate as electrolyte.

As soon as the liquor had become sat. with the sulphates of iron and nickel, the copper was precipitated by scrap iron, and the nickel separated from the iron as ammonium nickel sulphate. The latter salt was converted into nickel sulphate.

E. F. Günther found that the copper deposit is good so long as the conc. of the copper in the electrolyte does not fall below 1 per cent. Poor results were obtained with ammonium nickel sulphate as electrolyte owing to its low solubility. E. F. Günther also studied the deposition of nickel from soln. of nickel sulphate, using insoluble and soluble anodes—lead, zinc, and copper. Diaphragm cells were employed; two salts were placed in the anode compartment, one which formed a soluble and the other an insoluble salt with the anode metal regenerating at the same time as the first salt. In the experiments with lead anodes, sodium chlorate was used along with sodium chloride, sulphate, or chromate, which form insoluble lead salts. The deposits were good in all cases, but the regeneration with sodium sulphate was not so good. With copper anodes, the solvent and precipitant were respectively sodium sulphate and carbonate. The nickel deposit was fair. With zinc anodes, the solvent salt was sodium chloride or sulphate, and the precipitant was sodium carbonate. The nickel deposits were good. The precipitated salts were not good as pigments. W. Borchers devised a cell suitable for the production of pigments in the anode compartment, and of nickel in the cathode compartment.

In 1877, E. André proposed extracting nickel from nickeliferous matte, speiss, or alloys, cast in the form of anode plates, and suspended in dil. sulphuric acid. The current was to be so regulated that the copper alone deposited on the cathode of carbon or copper, leaving a soln. of iron and nickel sulphates in the electrolyte. The iron was to be precipitated from the electrolyte by evaporating the ammoniacal soln. in a current of air. The soln. of nickel sulphate was to be decanted from the precipitated ferric hydroxide, and worked up for nickel sulphate, oxide, or metal. In the last case, the nickel could be obtained by electrodeposition. W. Stahl, and B. Neumann suggested a modification of the process. G. A. Guess added a little glue to the electrolyte for the deposition of nickel, and recommended lead anodes, and a current density of 250 amps. per sq. ft. He also recommended adding finely-divided calcium carbonate in suspension to the electrolyte, and to suspend the cathode in a sack diaphragm. The calcium carbonate forms a double basic sulphate of copper which precipitates.

C. Hoepfner suggested several modifications of a process for extracting nickel electrolytically. In one modification of the process, the nickel ore was partially roasted to make the iron insoluble; and it was then extracted with a soln. of calcium chloride containing cupric chloride in the form of anode liquor from a subsequent stage of the process. The copper and nickel dissolved as cuprous and nickel chlorides respectively. The silver and iron were removed chemically, and the purified soln. of calcium, cuprous and nickel chlorides was electrolyzed to precipitate the copper. The remaining copper was removed chemically. The soln. of calcium and nickel chlorides on electrolysis with a sheet nickel cathode, and graphite anode gave a good deposit of nickel. The process was not successful; it was modified by J. Savelsberg and G. Wannschaff. E. Basse and G. Selve added organic substances—acetic or citric acid, glycerol, or dextrose—to neutral or slightly acid soln. of nickel, cobalt, iron, and zinc so as to prevent the precipitation of the hydrated oxides by alkalies. On electrolysis of the soln., made alkaline by the addition of potassium or sodium hydroxide, iron, cobalt, and zinc are deposited on the cathode whilst nickel either remains in soln. or is precipitated as hydrated oxide according to the conc. of the soln., or if the passage of the current is prolonged. Ammonium carbonate is added to the soln. to convert the free alkali into carbonate, and the soln. is then electrolyzed for nickel. D. de P. Ricketts electrolyzed a soln. of nickel and copper sulphates mixed with the sulphate of an alkali metal. Copper is deposited on the cathode and a sparingly soluble double sulphate collects at the bottom of the bath. U. le Verrier separated iron and nickel by electrolyzing a soln. containing ammonium nickel sulphate or ammonium nickel chloride and sodium chloride. The soln. was kept alkaline by means of a soluble hypochlorite. The anode was an alloy of nickel and iron. Hydrated ferric oxide was precipitated in the bath, and nickel deposited on the cathode. M. Kugel used hot nickel salt soln. acidified with perchloric, bromic, or sulphuric acid; the anodes were nickel matte. The acid content of the bath was maintained by the addition of a conc. soln. of a magnesium salt of the acid—*e.g.* magnesium sulphate for nickel sulphate. H. A. Frasch used for the

anode a copper plate on which rested coarsely crushed matte: a layer of sand over the matte served as diaphragm; a soln. of sodium chloride just covered the diaphragm, and over that a dil. soln. of sodium carbonate served as a cathode compartment. On electrolysis the chlorine formed at the anode acted on the matte, forming a soln. of nickel and copper chlorides which were alternately deposited electrolytically on the cathode.

In *T. Ulke's process* anodes of cast cakes of the bessemerized matte, and sheets of copper as cathodes are employed. The electrolyte was prepared by dissolving granulated matte in sulphuric acid, and it contained about 8 per cent. excess acid. The acid required replenishing from time to time. The copper deposited on the cathode, and copper and nickel dissolved at the anode; the anode slime contained the precious metals. When the percentage of copper in the soln. is small, the liquor is syphoned off, and the residual copper precipitated by sodium sulphide or by filtering through nickel sulphide. The iron in the soln. can be precipitated by adding hydrated nickel oxide. The nickel in the soln. can be precipitated as carbonate, or it can be deposited electrolytically. The precious metals in the slimes are recovered by the process of B. Moebius—**3.** 22, 3. In *D. H. Browne's process*, the copper-nickel alloy is cast into anode plates, and while copper is being deposited, copper sheets are used for the cathode. The electrolyte is a soln. of chlorides of copper and nickel, which is replenished by making it flow continuously through a tower where it comes in contact with nickel-copper matte, a soln. of sodium chloride and chlorine. The chlorine is generated from the nickel chloride soln. The copper is deposited first, and when the nickel in the electrolyte has attained a suitable concentration, the liquor is run off, the copper is first precipitated and then the iron. The soln. is then electrolyzed with carbon anodes and nickel sheet cathodes. The chlorine from the anodes passes up the tower indicated above. In *N. V. Hybinette's process* the copper-nickel matte is roasted, and the resulting oxides are leached with 10 per cent. sulphuric acid. This removes most of the copper but very little nickel. The residue is then heated with sulphuric acid to the temp. at which the sulphates become anhydrous, and again leached with dil. sulphuric acid. The residue is heated with hydrochloric acid and again leached with sulphuric acid. The solid residue is then smelted, and the metal is cast into anodes for electrolysis. A soln. of nickel sulphate is used as electrolyte. Cathodes consisting of iron plates thinly coated with graphite are employed, G. Haglund studied the process.

Modified processes have been discussed by T. Barton and T. B. McGhie, B. Bogitch, O. W. Brown, C. F. Burgess and C. Hambuechen, R. S. Carreras, A. Chalas, C. C. Cito, P. F. Cowing, F. L. Duffield, S. Fraser, S. Giertsen, J. H. Gillis, P. Goldberg, E. F. Günther, E. F. Günther and B. Franke, F. Haber, J. Heibling, W. Mc. A. Johnson, T. H. Kelley, R. G. Knickerbocker, G. Langbein, C. Langer, A. McKechnie and F. C. Beasley, H. M. Merriss, B. Mohr and C. B. Heberlein, L. Münzing, K. W. Palmaer and O. E. Griep, F. Peters, J. N. Pring, W. Salversberg, G. Schreiber, E. W. von Siemens and J. G. Halske, E. A. Sjöstedt and J. H. James, R. C. Stanley, T. Storer, J. Strap, R. L. Suhl and co-workers, J. C. Underwood, G. Vortmann, and H. L. Wells and J. C. King. The separation of cobalt and nickel has been discussed in connection with cobalt.

J. Garnier [8] treated fused nickel matte in an earthenware tube provided with carbon electrodes, with a current of 23 ampères at 10 volts, and found that the conductivity of the mixture remained very regular, but the voltage gradually diminished, although the temp. of the furnace was practically constant. The following table gives the composition of the original substance and of the products round the anode and cathode after passing the current for an hour and then cooling slowly:

	Sulphur	Iron	Nickel	Copper
Original substance . . .	21·10	33·30	16·30	29·00 per cent.
Anode product . . .	16·60	35·40	5·13	39·90 ,,
Cathode product . . .	4·70	49·10	19·10	26·13 ,,

The sulphur is, to a large extent, eliminated probably as carbon disulphide, and the remainder is concentrated at the anode. The quantity of nickel increases

from the anode to the cathode, whilst that of copper increases in the reverse direction. The iron, on the whole, tends to accumulate at the cathode. C. T. Henning discussed the electric smelting of nickel ores.

The impurities in commercial nickel.—Formerly, coarse nickel might contain 60 to 90 per cent. of nickel, but to-day the metal is extracted from a variety of ores and it contains 98 to 99 per cent. of nickel. The most common impurities are cobalt, copper, iron, zinc, sulphur, arsenic, silicon, carbon, and magnesium, whilst lead, antimony, manganese, and aluminium may be present. Commercial nickel appears on the market as (*a*) grains, cubes, rondelles, or powder reduced at a relatively low temp. from nickel oxide, and not fused in the process; (*b*) nickel deposited in concentric layers from nickel carbonyl and not fused in the process; (*c*) nickel deposited electrolytically as cathode sheets; (*d*) nickel made by reducing the oxide above the m.p. of the metal, and casting it, without deoxidation, in the form of blocks; or pouring it into water, when it appears in the form of shot; (*e*) malleable nickel prepared by reduction from the oxide above the m.p. of the metal, and mixed with some deoxidizer before it is poured or teemed into ingots or manufactured into rods, sheet, strip, wire, tubes, etc.

In illustration of the composition of earlier examples of coarse nickel, C. Schnabel gave for the percentage composition of samples from I, Joachimsthal; II, Klefva; and III, Schladming:

	Ni	Cu	Fe	Co	As	S	SiO_2
I .	71·4–86·5	0–18·9	0·2–1·3	0·9–12·0	0 –0·06	0–0·1	0–3·5
II .	83 –90	1·3– 2·0	0·2–0·4	5·5–11·2	—	0·7–1·4	0·7–0·9
III .	86·7–88	1·8– 1·9	1·8–1·9	6·8– 7·4	0·7–0·8	0·7–1·4	0–1·0

The Klefva nickel also contained 0·9 to 2·0 per cent. of Na; and the two other samples were reported to contain respectively 0·06 to 1·6 and 0 to 0·8 per cent. of residue insoluble in acids. Analyses were reported by R. Fresenius,[9] W. E. Gard, C. E. Guillaume, R. A. Hadfield, F. Heusler, A. Hollard, A. Hollard and L. Bertiaux, J. H. James and J. M. Nissen, A. Julien, A. Köbrich, J. L. Lassaigne, P. D. Merica, L. Moissenet, H. Nissenson and A. Mittasch, J. J. Pohl, P. Reiman, W. von Selve, S. P. L. Sörensen, L. Thompson, and P. Weselsky.

Table I includes a selection, made somewhat at random, of a dozen examples

TABLE I.—THE PERCENTAGE COMPOSITION OF COMMERCIAL SAMPLES OF NICKEL.

	Ni	Co	Cu	Fe	C	S	Si
Norway . .	99·52	0·89	0·6	0·36	—	—	—
Canadian . .	99·80	—	0·01	0·12	—	—	—
Orford . . .	99·82	0·80	0·01	0·14	—	trace	—
Electrolytic . .	99·80	—	0·05	0·15	nil	nil	nil
Mond . . .	99·86	nil	0·008	0·040	0·030	nil	0·007
New Caledonian .	98·11	—	0·50	1·60	—	—	0·13
Cubes . . .	99·28	—	0·065	0·32	0·41	—	—
Rondelles . .	99·20	—	—	0·45	0·15	0·01	0·10
Grain . . .	99·17	—	0·13	0·51	—	—	—
Shot . . .	99·25	0·25	0·06	0·50	nil	0·014	nil
Ingots . . .	99·10	0·80	0·13	0·50	0·10	0·60	0·10
Sheet . . .	97·99	0·88	0·12	0·49	—	—	—

from the reports of D. H. Browne and J. F. Thompson, the Report of the Royal Ontario Nickel Commission, and the Circular of the Bureau of Standards. The subject was discussed by F. Mylius, who showed that technical nickel can be obtained with only 0·029 per cent. of impurities. The presence of cobalt as an impurity was discussed by R. J. McKay, and W. R. Barclay. The "ingots" had 0·015 per cent. As and 0·015 per cent. Sn and Sb; and the "sheet" 1·32 per cent. of manganese. The "impurities" have not been determined in all cases. In some

cases the reported Ni includes both cobalt and nickel. No particular conclusion as to the relative merits of samples from different localities is to be drawn from these data. Another table could have been just as easily compiled to show another order of merit. The data are to be taken as a whole, showing what may be expected from modern commercial nickel. Vessels for melting nickel were studied by L. Jordan and co-workers, and are discussed in connection with iron.

The purification of nickel.—Nickel can be refined electrolytically or by dry processes. The commercial electrolytic processes have been indicated above. In some cases, efforts are directed to obtaining a purified nickel oxide, and reducing that to the metal. According to C. Schnabel,[10] the purification of nickel by an oxidizing fusion in a kind of puddling furnace, removes only those impurities which are more readily oxidized than is nickel itself—*e.g.*, carbon, silicon, and iron. P. Manhès, and P. C. Gilchrist and S. G. Thomas exposed the metal to the action of oxidizing agents like air, nitre, etc., at a red-heat. J. Garnier proposed to remove sulphur by heating the metal in a reverberatory furnace with a bed of powdered limestone which, giving off carbon dioxide, agitates the metal, and the lime takes up the sulphur. R. Fleitmann used manganese to remove sulphur from the metal. P. Manhès removed sulphur by heating the metal with a mixture of lime and calcium chloride on a basic hearth in a reverberatory furnace. W. S. Smith and co-workers used lime and silica with some fluorspar for desulphurizing the molten metal; O. Lellep, and H. Watle used gases containing oxygen. The Berndorfer Metallwarenfabrik removed carbon by soaking cubes of nickel, reduced at a moderate heat, in a 4 per cent. soln. of alkali manganate or permanganate, and fused the product at a high temp. J. Garnier removed iron by smelting the metal with quartz as a flux. L. Jordan and co-workers recommended crucibles made from purified magnesia, for melting nickel.

When nickel is fused in crucibles or furnaces during the reduction of nickel oxide, the product may contain nickel oxide which remained dissolved in the metal as in the corresponding cases of copper and iron. This makes the nickel brittle. Carbon monoxide may be absorbed by the nickel, making the metal inclined to springiness; and nickel cyanide may be formed which, according to T. Fleitmann, makes the metal brittle. T. Fleitmann showed that if magnesium be added to molten nickel, these three impurities are decomposed. The refining of nickel was described by C. Schnabel, E. T. Richards, G. Masing and L. Koch, K. Styffe, and R. Fleitmann. From one-twentieth to one-eighth per cent. of magnesium may suffice, and the resulting metal—the so-called **malleable nickel**—is ductile, and it can be welded to itself or to iron and steel. Without some such purifying agent nickel, in general, cannot be rolled or forged. The amount of magnesium required can in some cases be reduced if hydrocarbons, carbon monoxide, or hydrogen be first blown through the metal. C. Schnabel reported the following results of the fusion of nickel with 1·5 ozs. of magnesium per 70 lbs. of metal in graphite crucibles lined with fireclay:

		Ni	Co	Fe	Cu	Si or SiO_2	C	S	Mg
I	Before .	97·87	1·45	0·45	0·10	0·19	trace	0·05	—
	After .	98·24	1·09	0·36	0·10	0·06	-	—	0·11
II	Before .	98·21	1·19	0·25	0·07	0·24	trace	trace	—
	After .	98·38	1·04	0·32	0·07	0·07	—	—	0·12

Other substances can be used, but less advantageously, than magnesium—*e.g.* aluminium, calcium, or a calcium-zinc alloy; black flux and coal have been tried, and here it is thought that the deoxidation is due to the formation of the vapour of potassium. The Société Anonyme Fonderie de Nickel et Métaux Blancs recommended aluminium or potassium cyanide. J. Garnier, and G. A. Boeddicker recommended, say, 1·5 to 3 per cent. of manganese as a purifier; F. Osmond, R. Fleitmann, G. Selve and F. Lotter proposed mixing manganese dioxide with the nickel oxide before the oxide is reduced; P. D. Merica used aluminium. H. C. C. de Ruolz, H. C. C. de Ruolz and A. L. M. de Fontenay tried phosphorus to deoxidize

nickel, but J. Garnier said that if over one-three thousandth part of phosphorus is present the nickel becomes harder, but less malleable; he therefore recommended a phosphor-nickel with about 6 per cent. of phosphorus as a deoxidizer. L. Schmal used a magnesium-manganese phosphide; this was discussed by C. Roberts.

P. D. Merica and R. G. Waltenberg showed that the magnesium, etc., act not by removing oxygen, for they found that the presence of carbon, silicon, iron, copper, arsenic, cobalt, manganese, and oxygen had little effect on the malleability of nickel, and similarly also with the occluded gases carbon monoxide and dioxide, hydrogen, and nitrogen. They found that sulphur, and sulphur alone, is responsible for the brittleness of ordinary nickel. Commercial nickel with less than 0·005 per cent. of sulphur is malleable both hot and cold, before and after remelting, and without any addition of manganese, and magnesium. As little as 0·01 of sulphur makes the metal almost completely non-malleable. This profound effect is due to the formation of a film of nickel sulphide which surrounds each metallic grain of nickel and lowers the intercrystalline cohesion of the mass even at low temp. The addition of 0·5 to 1·0 per cent. of manganese improves the malleability of nickel with 0·01 per cent. of sulphur; and the addition of 0·5 to 0·10 per cent. of magnesium completely restores its malleability. The facts also apply to monel metal.

A number of wet processes have been employed for purifying nickel. Thus, H. St. C. Deville [11] evaporated the nitric acid soln. of the metal in order to remove the iron; the residue was taken up with water and treated with hydrogen sulphide. The filtrate was boiled and filtered to remove sulphur, and then treated with oxalic acid and boiled a few minutes; nickel oxalate separates from the acid soln. The oxalate was then treated in a lime crucible while protected from air. The oxalate can also be reduced by heating it in dry air, and then in hydrogen. Modifications of the process were employed by R. Schneider, H. Baubigny, and C. Zimmermann. L. Thompson finally fused the metal under borax in a fireclay crucible. Methods of purification were also employed by F. Claudet, G. Delvaux, P. Dirvell, N. W. Fischer, P. J. Robiquet, F. Gauhe, A. Guyard, M. Ilinsky and G. von Knorre, A. Laugier, J. von Liebig, A. Patera, R. Phillips, F. Pisani, F. Rose, H. Rose, R. Schneider, S. P. L. Sörensen, A. Terreil, and L. Thompson. The separation of nickel and cobalt is discussed in connection with the latter element.

Elaborate methods of purification have been employed in atomic weight determinations (*q.v.*); thus, C. Winkler dissolved the carbonate in hydrochloric acid, heated the soln. repeatedly with bleaching powder to precipitate iron and cobalt oxides; precipitated arsenic and copper by hydrogen sulphide; heated the liquid freed from hydrogen sulphide with sodium carbonate; dissolved the washed carbonate in hydrochloric acid and evaporated the soln. to dryness; sublimed the nickel chloride in a current of dry chlorine; and finally reduced the chloride in a current of purified hydrogen. T. W. Richards and A. S. Cushman treated a soln. of the commercial salt (or nickel derived from the carbonyl) with hydrogen sulphide; boiled the filtrate to drive off the excess of hydrogen sulphide; oxidized the soln. with a few drops of nitric acid, and made the soln. alkaline with ammonia; the filtered liquid was treated with hydrogen sulphide; the precipitated nickel sulphide was washed with hot water and dissolved in hydrochloric acid; the filtrate was evaporated to dryness and taken up with hot water; the clear soln. was twice fractionally precipitated as hydroxide by the method of E. F. Anthon; the hydroxide was transformed into bromide by heating it in a porcelain tube in a current of hydrogen bromide; and the sublimed bromide was then purified as nickel hexamminobromide. C. Winkler obtained the metal by the following electrolytic process from the purified sulphate:

An aq. soln. of nickel sulphate with 32·84 grms. of nickel per litre was prepared, and 200 c.c. mixed with 30 grms. of ammonium sulphate, 50 grms. of aq. ammonia of sp. gr. 0·905, and 250 c.c. of water. The cathode was a polished nickel plate 9·7 cms. by 7·9 cms. and the anode was a piece of platinum foil of the same dimensions. A current of 0·8

ampère at 2·8 volts was employed. As soon as the nickel deposit had acquired a certain thickness, it curled off the cathode in flakes of white lustrous metal with a yellowish tint. The metal had a high degree of purity since repeated heating in hydrogen failed to produce any loss of weight.

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§ 4. The Preparation of Nickel

At the beginning of the nineteenth century, P. Berthier,[1] J. B. Richter, and O. L. Erdmann prepared the nickel in the laboratory by heating nickel oxide or carbonate, alone, or mixed with charcoal, or made into a stiff paste with oil, with or without a layer of glass, in a covered crucible, and at the temp. of a blast-furnace. The nickel dissolves a small quantity of carbon. If the temp. be kept as low as possible, a grey, porous mass of nickel is produced with very little carbon. J. von Liebig and F. Wöhler, A. Laurent, G. Charpy, G. Magnus, G. Grassi, W. N. Ipatéeff, and C. Künzel obtained nickel in an analogous manner. E. W. von Siemens and J. G. Halske reduced the oxide with carbon in an electric furnace. E. D. Clarke observed that nickel oxide is reduced to the metal in the oxyhydrogen flame. Nickel oxide is also reduced by heating it in a current of hydrogen, and, according to W. Müller, a suboxide—*vide infra*—is formed at 194°, and the reduction is complete at 270°. M. Mayer and V. Altmayer showed that nickel reduced in hydrogen absorbs much gas—*vide infra.* W. N. Ipatéeff found that soln. of nickel salts are reduced to the metal when heated under press. in hydrogen. Thus, with hydrogen at 100 atm. press. $0{\cdot}2N$-$NiSO_4$ deposits nickel at 186°, and of a $0{\cdot}2N$-soln. of nickel acetate, at 168°. J. von Liebig and F. Wöhler, and A. Laurent reduced the oxide by heating it in a current of carbon monoxide ; and I. L. Bell noted that at a high temp. much carbon is formed.

J. W. Döbereiner, and J. J. Berzelius prepared the metal by heating to redness nickel oxalate, or ammonium nickel oxalate under a layer of powdered glass free from heavy metal. E. Péligot, P. Schützenberger, and H. Rose obtained lustrous crystals of nickel by heating nickel chloride in a current of hydrogen ; and F. Vorster by heating the chloride in a current of dry ammonia. L. Mond and co-workers, and M. Berthelot prepared the metal by heating nickel carbonyl to 200°. A. C. Becquerel found that copper in a soln. of sodium nickel chloride precipitates nickel ; Z. Roussin, that magnesium precipitates nickel from slightly acidified soln. of nickel salts ; A. Commaille, that magnesium precipitates nickel from soln. of nickel sulphate ; and A. Merry, and J. L. Davis, that nickel is precipitated by zinc from ammoniacal soln. of its salts. H. Moissan obtained the metal by distilling nickel-amalgam in a current of hydrogen. A. Damour found that zinc amalgam precipitates nickel from neutral soln. of zinc salts, and forms an amalgam. C. Mème, and F. Stolba found that a soln. of nickel sulphate and zinc chloride deposits nickel on iron in contact with zinc ; but F. M. Raoult observed no deposit of nickel from acidic or neutral, hot or cold soln. of nickel salts in contact with a nickel-gold couple. For the production of nickel from nickel carbonyl, *vide supra.* H. E. Fierz and H. A. Prager, A. E. van Arkel, and C. Müller and W. Schubardt used this process.

Nickel is deposited on the cathode during the electrolysis of ammoniacal, neutral, or acidic soln. of its salts, and, as shown by R. Böttger,[2] J. M. Merrick, and C. Winkler, the metal so obtained has a high degree of purity, but, as shown by J. M. Merrick, it may be contaminated with oxides.

In 1842, R. Böttger showed that dense and lustrous deposits of nickel could be obtained by the electrolysis of a soln. of nickel and ammonium sulphate, or of an ammoniacal soln. of nickel sulphate. He also emphasized many valuable qualities of the nickel deposits, which attracted attention only after R. Böttger's work had been forgotten, and the facts discovered anew. In 1868, W. H. Remington patented a process for the electrodeposition of nickel ; in 1869, I. Adams patented the use of nickel ammonium sulphate as an electrolyte in conjunction with cast nickel anodes ; and in 1871, N. S. Keith patented the use of tartrates—*e.g.*, Rochelle salt—in the electrolytic bath. At ordinary temp., the use of a current density of about 5 amp. per sq. ft. was considered to give the best results. The corresponding rate of deposition was comparatively slow. The use of higher temp. hastened the rate of

deposition, but this was considered inconvenient under manufacturing conditions. In order to produce a higher concentration of nickel in the bath than is possible with ammonium nickel sulphate, which has a relatively low solubility, as pointed out by A. Brochet, a portion of the complex salt was replaced by the simple salt nickel sulphate. In 1878, E. Weston showed that the ammonium sulphate could be advantageously omitted if boric acid be added along with nickel sulphate. A higher rate of anodic corrosion was then needed to enable higher rates of deposition to be employed. W. D. Bancroft pointed out that a relatively small proportion of a soluble chloride in the bath would greatly improve anodic corrosion, and electrolytes containing nickel sulphate, boric acid, and a soluble chloride came into favour. In 1916, O. P. Watts found that with soln. containing per litre 240 grms. of nickel sulphate, 20 grms. of boric acid and 20 grms. of nickel chloride gave good deposits with a current density of 200 amps. per sq. ft., and under commercial conditions, 50 to 100 amps. per sq. ft. The subject was studied by V. I. Lainer and co-workers, N. V. Hybinette, C. C. Downie, R. L. Suhl and co-workers, W. A. Mudge, A. H. W. Aten and co-workers, G. A. Guess, N. R. Laban, and C. G. Fink and F. A. Rohrman discussed the conditions favourable to the preparation of pure, electrolytic nickel.

Although the equilibrium potential of nickel in N-$NiSO_4$ at room temp. is about $-0{\cdot}25$ volt, a large excess of anodic polarization is necessary to inaugurate the dissolution $Ni+2\oplus \rightarrow Ni^{\cdot\cdot}$. Thus, E. P. Schoch found a nickel anode in N-$NiSO_4$ at 26° dissolves only at current densities below 0·036 amp. per sq. dm. If this value be exceeded, the anode becomes passive, and oxygen is evolved when the potential is about $+0{\cdot}28$ volt, *i.e.*, an excess polarization of 0·53 volt. The passivity decreases as the temp. is raised or in the presence of Cl'-ions or $H^{\cdot}$-ions. Hence, by raising the temp., or in acidic soln., or soln. with a soluble chloride, a nickel anode can be subjected to greater current densities without the anode assuming the passive state. As shown by O. W. Brown, the potentials at the anode vary with the physical state of the metal; thus electrolytic nickel requires a high potential, and cast nickel with its surface roughened dissolves more readily than any other form of anode. Wrought iron of uneven structure may yield slimes containing undissolved metal. Since the equilibrium potential of nickel in N-$NiSO_4$ is $-0{\cdot}26$ volt, nickel cannot be deposited from soln. containing even moderate quantities of free acid. The work of E. P. Schoch, and A. Schweitzer shows that the hydrogen overvoltage of nickel at room temp. is at least 0·2 volt, but this is counterbalanced by the fact that the slowness of the reaction $Ni^{\cdot\cdot} \rightarrow Ni+2\oplus$ at the cathode necessitates a higher cathodic polarization than corresponds with the equilibrium value. N. A. Isgarisheff and C. M. Ravikovitsch found that the cathode polarization with nickel chloride is affected by the addition of various chlorides in the order $CdCl_2 < AlCl_3 < LiCl < CoCl_2 < MgCl_2 < NiCl_2 < NaCl < KCl < CaCl_2 < SrCl_2 < NH_4Cl < BaCl_2 < ZnCl_2$. At room temp., 16°, A. Schweitzer found that the following cathode potentials are needed for the deposition of nickel from N-$NiCl_2$ in an atm. of hydrogen, and an equilibrium potential about $-0{\cdot}31$ volt:

Current density .	0	0·01	0·03	0·06	0·11	0·9 amp. per sq. dm.
Cathode potential	−0·31	−0·462	−0·486	−0·510	−0·535	−0·645 volt.

Hence, the excess polarization increases with the current density, but it decreases with a rise of temp., being only about 0·1 volt at 90°. It therefore follows that the $H^{\cdot}$-ion conc. must be low, or the current efficiency for the deposition of nickel will be low. There is a Scylla to this Charybdis because if the $H^{\cdot}$-ion conc. be too low, basic salts may be formed, the bath fouled, and the quality of the deposit impaired.

The effect of the $H^{\cdot}$-ion conc. on the deposition of nickel has been studied by M. Ballay, J. Barbaudy and A. Petit, J. Barbaudy and co-workers, W. Blum and N. Bekkedahl, W. Blum and M. R. Thompson, A. E. Brewer and G. H. Montillon, C. E. Clindinin, A. K. Graham, L. E. and V. E. Grant, H. E. Haring, R. Harr, J. C. Kretchmer, H. Kurrein, W. Lockerbie, D. J. MacNaughtan and R. A. F. Hammond, D. J. MacNaughtan

and co-workers, H. B. Maxwell, G. H. Montillon and N. S. Cassel, W. A. Mudge, J. B. O'Sullivan, H. C. Parker and W. N. Greer, L. C. Parn, W. H. Phillips, W. M. Phillips, K. Pitschner, A. Regmunt, R. G. Suman, W. A. Taylor, M. R. Thompson, S. Triandafil, and O. P. Watts—*vide infra*.

W. Wernicke observed that nickel peroxide is formed at the anode in alkaline soln.—say, an alkaline soln. of sodium tartrate and nickel hydroxide. The reaction in the nickel-plating bath was studied by A. Brochet, H. S. Carhart, F. Förster and F. Kruger, R. L. Dorrance and W. C. Gardiner, F. Förster, P. K. Frölich and G. L. Clark, and F. E. Lathe. C. Russo studied the rate of anodic solution in N-H_2SO_4.

There is a difficulty in obtaining thick deposits of nickel at ordinary temp. With other than low current densities, the deposit peels off in thin flakes, and a coherent film cannot be obtained. In the case of iron, a similar effect has been attributed to the irregular occlusion of hydrogen by the metal producing strains in the deposit; but K. Engemann showed that the solubility of hydrogen in nickel is probably too low to produce such an effect, and he attributed the phenomenon to the presence of traces of iron in the electrolyte depositing on the cathode more readily than nickel, so that the first layers contain a higher proportion of iron than the subsequent layer. As a result, strains are set up and flaking occurs. He obtained no flaking with electrolyte and anode quite free from iron. A low temp., a low $H^{\cdot}$-ion conc., and a high current density all favour an irregular deposition of iron and also flaking. F. Förster obtained good thick deposits at a higher temp., say 50° to 90°, even when the current density is high, say 2·5 amps. per sq. dm. Hot soln. were also recommended by M. Kugel, G. Langbein, W. S. Barrows, R. F. Clark, W. G. Horsch, and A. E. Shepherd.

F. Förster showed that compact and thick deposits, used with crude nickel anodes, can be obtained at temp. between 50° and 90°. A. Classen recommended hot, neutral soln. of nickel sulphate and ammonium oxalate for the electrodeposition of nickel. F. Förster obtained much better results with sulphate soln. than with chloride soln. as electrolytes. Very little separation was effected with nickel, iron, and cobalt, but carbon, silicon, copper, and manganese could be eliminated. When the proportion of iron is high, the deposit curls off the cathode. With chloride soln. bubbles of hydrogen form more readily on the cathode, and these tend to produce warty deposits. N. Fedotieff and R. Kinkulsky, and E. F. Kern and F. G. Fabian examined the effect of varying concentrations of acid, temp., and current density on the current efficiency, and on the nature of the deposits; and their results with soln. containing 8 per cent. of Ni are in part summarized in Table II. The heavy deposits are due to the formation of basic salts, and this is particularly marked with neutral soln. of nickel chloride.

"Conducting" salts are added to the bath to decrease the electrical resistance of the bath. The resistance of the bath was studied by R. L. Dorrance and W. C. Gardiner, A. E. Nicol, H. E. Haring, L. D. Hammond, C. W. Heil, and E. F. Kern and M. Y. Chang. The effect of superposing an alternating current on the direct current employed in the deposition of nickel, and its alloys, was studied by H. C. Cocks, A. Copperado, N. A. Isgarisheff and S. Berkmann, W. G. Ellis, V. Kohlschutter and H. Schodl, and S. A. Tucker and H. G. Loesch; and the effect of high current densities by N. R. Laban. G. Langbein considered that potassium, sodium, magnesium, or ammonium salts are best suited for this purpose, but the ammonium chloride is not good, and that sodium acetate, barium oxalate, ammonium nitrate, ammonium-alum, and the like are unsuitable. In general, the additions of chlorides, and baths prepared with nickel chloride or nitrate, are not suited for the solid nickeling of iron. P. A. Nichol and O. P. Watts found the use of nitrates objectionable. D. W. Robinson emphasized the use of magnesium sulphate in raising the conductivity of the soln., improving the character of the deposit, increasing the weight deposited in a given time, dissolving the anodes more evenly, and avoiding pitting. Small proportions of fluorides or chlorides—sodium,

TABLE II.—THE EFFECT OF BATH CONDITIONS ON THE ELECTRODEPOSITION OF NICKEL

Electrolyte addition	Temp.	Current Density (amp. per sq. ft.)	$NiCl_2$		$NiSO_4$		$NiSiF_6$	
			Voltage (volt.)	Current Efficiency (per cent.)	Voltage (volt.)	Current Efficiency (per cent.)	Voltage (volt.)	Current Efficiency (per cent.)
0·5*M*-free acid .	20°	10	0·49	3·20	0·89	0·86	0·96	0·78
	40°		0·36	1·25	0·65	0·62	0·78	1·64
	60°		0·21	1·01	0·42	0·39	0·61	1·80
0·1*M*-free acid .	20°	10	0·73	62·6	0·91	1·50	0·82	2·20
	40°		0·52	79·0	0·78	1·60	0·83	4·90
	60°		0·35	71·0	0·51	1·50	0·61	4·80
0·05*M*-free acid .	20°	12	0·86	67·2	0·97	0·0	1·02	7·8
	40°		0·53	75·7	0·79	0·7	0·90	7·1
	60°		0·44	80·7	0·61	2·8	0·82	8·5
Neutral .	20°	10	0·78	96·6	1·50	102·2	1·05	92·1
	40°		0·59	99·4	1·35	106·9	0·94	92·4
	60°		0·44	99·2	0·88	101·1	0·73	89·8
Neutral .	20°	20	1·06	91·2	3·45	—	1·45	96·8
	40°		0·73	94·7	2·30	—	1·24	100·0
	60°		0·64	88·3	1·40	—	1·01	90·3
0·5*M*-Na salt .	20°	20	1·02	90·2	3·12	10·2	—	—
	60°	60	0·58	99·7	0·96	99·8	—	—

ammonium, magnesium, or nickel—however, act by reducing the tendency of the anode to become passive, and by favouring the corrosion of the anode. The use of baths of nickel cyanide in soln. of potassium cyanide, recommended by R. H. Marshall, and P. and Q. Marino, were found by G. Langbein to give poor deposits. Whilst the presence of a dil. acid is desirable, the addition of strong acids is to be avoided, but weak acids, like citric or acetic acid, etc., can be recommended. The salts of the organic acids act by regulating the acidity of the bath, by dissolving basic salts of nickel, iron, etc., and reducing the rate of deposition of nickel by more positive metals as in the electroplating of zinc and of its alloys. J. Powell recommended benzoic acid, and E. Weston, J. Barbaudy and A. Petit, E. M. Baker, etc., boric acid. The boric acid has a favourable effect in producing silvery-whiteness; prevents the formation of basic salts, and it makes the deposit more adherent, softer, and flexible. The yellowness of electrodeposited nickel is attributed to the presence of basic nickel salts, but this has not been proved. G. Langbein, and F. Förster said that the deposit with boric acid is harder than it is with a free organic acid, and that they cannot be made so thick as is readily attained with the nickel ethyl sulphate baths. L. D. Hammond showed that boric acid acts by maintaining more uniformly the $H^{\cdot}$-ion conc. of the soln., and that although good deposits can be obtained from soln. slightly acidified with strong or weak acids, none of the acids were so good as boric acid for continued service. The addition of glycerol is claimed by P. and Q. Marino, J. A. Murphy, and H. Gardner to act as a depolarizer and allow lustrous nickel deposits to be produced of great homogeneity. G. Langbein was unable to produce better deposits in the presence of glycerol than in its absence. The addition of carbon disulphide to nickel baths is said to prevent the nickel deposit from becoming dull when it has attained a certain thickness, but G. Langbein found no advantage attends the use of this agent. The general subject, and the use of glycine were discussed by G. Fuseya and co-workers; and the effect of foreign metals, by B. Setlik.

According to I. Adams, in the search after solutions from which metals can be practically deposited, the rule-of-thumb method prevailed and had to prevail. In the search for a practical silver-plating solution, doubtless hundreds of silver salts were tried before the rather out-of-the-way double cyanide of silver and potassium was found. In the case of untried metals, the experimenter could not safely draw

inferences from similar combinations. There were no rules, and few theories to guide, and it is much the same to-day. All this means that in the quest for solutions suitable for electroplating, the method of trial and failure, hit or miss, has to be followed. J. M. Merrick reported trials with ammoniacal soln. of nickel chloride, sulphate, and nitrate, as well as with the complex salts with the corresponding ammonium or potassium salts. A. Smee, and J. M. Merrick tried nickel acetate; J. M. Merrick, potassium nickel cyanide; E. F. Kern and F. G. Fabian, nickel fluosilicate, dithionate, chloride, and sulphate; J. Powell, L. E. Stout and C. L. Faust, J. H. Potts, and A. Watt, acetates, benzoates, chlorides, citrates, lactates, tartrates, and formates; G. Gore, selenate; A. Hollard, dichromates, and pyrophosphates; M. le Couteulx, ammonium persulphate; D. J. MacNaughtan and R. A. F. Hammond, chromic acid or chromic sulphate; C. P. Madsen, W. G. Ellis, and the Madsenell Corporation, hydrogen dioxide, and chlorine; E. A. Ollard, ozone or ozonized air; W. Blum, and Q. Marino, fluorides; P. and Q. Marino, sulphanilic acid, borotartrates, glyceroborates, glycerobenzoates, borobenzoates, phosphates, bromates, glucose, borocitrate, and borotartrate; A. Classen, liquorice root; V. Garin, gelatin or albuminous substances; E. N. Todd and W. R. King, gum tragacanth; N. A. Isgarisheff and S. Berkmann, gelatine; and B. H. Divine, glue. E. F. Kern studied the function of addition agents in electrolytes, and K. Pitschner, the buffer action.

Numerous recipes for baths for the electrodeposition of nickel have been published. For instance, W. R. Barclay and C. H. Hainsworth recommended $(NH_4)_2Ni(SO_4)_2.6H_2O$, 375 grms.; $NiSO_4.7H_2O$, 94 to 125 grms. made up to 5 litres with water at 20°, using a current density of 5 amps. per sq. ft. initially at 5 volts and subsequently falling to 3 volts or even less. They also recommend $(NH_4)_2Ni(SO_4)_2.6H_2O$, 312 grms.; $NiSO_4.7H_2O$, 125 grms.; potassium or sodium chloride, 31 to 47 grms. made up to 5 litres with water, and worked at a current density of 10 amps. per sq. ft. O. P. Watts recommended a soln. containing $NiSO_4.7H_2O$, 240 grms.; $NiCl_2.6H_2O$, 20 grms.; and boric acid, 20 grms. per litre. E. A. Ollard gave $NiSO_4.7H_2O$, 300 grms.; H_3BO_3, 25 grms.; NaF, 6 grms.; and $NiCl_2.6H_2O$, 2 grms. per litre, with a current density of 15 to 70 amp. per sq. ft., and $P_H = 5{\cdot}7$ to $5{\cdot}9$.

Other recipes or processes have been recommended by I. Adams, K. Altmannsberger, R. Appel, E. M. Baker, M. Ballay, G. B. Barham, C. W. Bennett and co-workers, A. F. Berry, E. Blasset, W. Blum and co-workers, M. Boden, B. Bogitch, H. E. Boughay, E. Breuning and O. Schneider, P. S. Brown, T. Brown, A. Cachemaille, D. F. Calhane and A. L. Gammage, J. Canac and E. Tassilly, E. R. Canning, R. Carl, C. F. Chandler, M. Chirade and J. Canac, R. F. Clark, A. Copperado, S. Cornell, S. O. Cowper-Coles, H. D. Cunningham, J. W. Cuthbertson, G. Dary, N. H. M. Dekker, M. Delval and M. Pascales, C. H. Desch and E. M. Vellan, E. J. Dobbs, F. M. Dorsey, H. H. Dow and co-workers, T. A. Edison, G. Eger, C. H. Eldridge, D. T. Ewing and co-workers, T. Fearn, S. Field and A. D. Weill, L. C. Flowers and J. C. Warner, B. Foss, P. K. Frölich and G. L. Clark, J. Galibourg, H. Gardner, V. Garin, E. P. M. Gat and E. M. L. Carrière, S. Gordon, C. B. Gordon-Sale, P. A. Govaerts and P. M. Wenmaekers, C. H. R. Gower and S. O'Brien, A. K. Graham, G. A. Guess, L. Guillet and M. Gasnier, V. M. Guskov and A. Z. Rivkind, J. Haas, G. Haglund, L. D. Hammond, H. E. Haring, W. E. Harris, W. J. Harshaw and co-workers, R. J. Hazucha, C. Heberlein, S. Herrick, M. Hess, G. B. Hogaboom, A. Hollard, A. W. Hothersall, W. E. Hughes, N. V. Hybinette, H. Jacobi, Y. Kato, M. de Kay Thompson, R. Kayser, E. F. Kern and co-workers, H. Kersten, W. R. King, F. Kirschner and J. Hess, F. V. Knauss, W. G. Knox, J. C. Kretchmer, L. J. Krom, H. Kurrein, N. R. Laban, V. I. Lainer and co-workers, E. P. Later, F. C. Lea, T. Ledin, F. J. Liscomb, E. G. Lovering, D. J. MacNaughtan and co-workers, C. P. Madsen, P. Marino, Q. Marino, M. Martin and M. Delamotte, F. C. Mathers and co-workers, I. Matuschek, A. Mazuir, Madsenell Corporation, B. Mendelsohn, P. D. Merica, O. Meyer, E. Monel, J. A. Murphy, L. F. Nelissen, E. Newbery, W. Obst, E. A. Ollard, L. C. Pan, A. Passalacqua, W. P. Pfanhauser, W. M. Phillips, E. Potter, J. H. Potts, J. Powell, C. H. Proctor and O. J. Sizelove, M. Quentin, A. V. Re, R. Riedal, D. W. Robinson, F. P. Romanoff, A. Rosenberg, S. W. Rowsbar, R. Saxon, M. Schlötter, L. Schulte, O. Silvestri, S. C Smith, R. C. Snowden, Société Anonyme Le Nickel, B. C. Soyenkoff, H. Stäger, E. E. Stafford, J. Stedman, W. W. de Sveschnikoff and H. E. Haring, A. Sviguin, E. Tassily, F. T. Taylor, H. T. Ter Doest, C. T. Thomas and W. Blum, M. R. Thompson, E. N. Todd and W. R. King,

T. H. Turner, J. Unwin, W. Voss, E. A. Vuilleumier, J. Walters, I. W. Wark, T. T. B. P. Warren, O. P. Watts, H. Webb and S. O'Brien, W. H. Webber, E. E. B. Weigle and E. Janez, E. Werner, and T. D. Yensen. I. W. Wark discussed the energy efficiency of the electrolytic process.

In the so-called *black nickelling*, instead of trying to obtain a silver-white deposit, a black or dark brown coloured deposit is produced. The bath then employed contains some thiocyanate and arsenic. Thus, E. Blasset recommended a bath of ammonium nickel sulphate 12 ozs., potassium thiocyanate 2·75 ozs., copper carbonate 2 ozs., and arsenious acid 2 ozs., made up with 95 galls. of water. The subject was discussed by G. B. Hogaboom and co-workers, J. Haas, A. Classen, W. S. Barrows, K. Tamaki, H. B. Maxwell, C. H. Proctor, R. H. Slater, J. Haas, O. P. Watts, and W. Blum. H. Kersten and J. Maas found that the structure of black nickel is amorphous.

In analytical work, nickel, as well as cobalt, can be deposited electrolytically from soln. of their double cyanides or oxalates, or from soln. of the sulphates mixed with alkali acetates, tartrates, or citrates, or from ammoniacal soln. E. F. Smith said that ammoniacal soln. are best adapted for the electrodeposition, and the presence of ammonium sulphate or sodium phosphate favours the separation. A rotating cathode may be employed. In illustration, H. Fresenius and F. Bergmann commended using as electrolyte 50 c.c. of a soln. of nickel containing 0·1233 grm. Ni, 100 c.c. of aq. ammonia of sp. gr. 0·96, 10 c.c. of a soln. of 305 grms. of ammonium sulphate per litre, and 100 c.c. of water. The electrodes can be 0·5 to 0·67 cm. apart; the current density 0·5 to 0·7 amp. per 100 sq. cm. at 2·8 to 3·3 volts at ordinary temp.; and the time required for a complete separation of the nickel was 4 hrs. The separation of nickel from copper, cobalt, and iron was studied by C. G. Fink and F. A. Rohrman. A. Glazunoff and J. Krieglstein discussed the iron content of electrodeposited nickel.

The subject was studied by R. Böttger, M. Boudreaux, A. Brand, E. D. Campbell and W. H. Andrews, M. S. Cheney and E. H. S. Richards, A. Classen, A. Classen and A. von Reis, A. Coehn and M. Glaser, K. Elbs, F. F. Exner, A. Fischer, A. Fischer and R. J. Boddaert, F. Förster and co-workers, R. von Foregger-Greiffenturn, H. Fresenius and F. Bergmann, E. Gaiffe, O. W. Gibbs, F. A. Gooch and H. E. Medway, L. Gräfenberg, P. Grésy, W. Hampe, M. Herpin, J. Herzog, M. Hess, A. Hollard, C. B. Jacobs, R. Kayser, C. A. Kohn and J. Woodgate, F. W. Küster, A. Kundt, E. Langbein, S. von Laszczynsky, C. Luckow, Mansfeldsche Berg- und Hüttendirektion in Ersleben, M. Martin and M. Delamotte, H. Meidinger, J. M. Merrick, T. Moore, R. Namais, P. Nauhardt, H. H. Nicholson and S. Avery, H. Nissenson and H. Daniel, W. Ohl, F. M. Perkin, F. M. Perkin and W. C. Prebble, O. Piloty, A. Riche, E. H. Riesenfeld, M. Roloff and E. Siede, M. Roloff and H. Wehrlin, J. E. Root, G. A. le Roy, F. Rüdorff, A. Schumann, G. P. Schweder, S. P. Sharples, A. Siemens, O. Silvestri, E. F. Smith and co-workers, R. C. Snowden, F. Stolba, W. T. Taggart, A. Thiel, H. Thomälen, B. Tougarinoff, C. Tubandt, G. Vortmann, T. T. P. B. Warren, J. Westerson, E. Weston, C. Winkler, G. C. Wittstein, F. Wrightson, and J. Zedner.

O. Meyer [3] showed that nickel may be deposited from a soln. of the chloride in alcohol; R. Taft and H. Barham, from soln. of nickel salts in liquid ammonia; R. D. Blue and F. C. Mathers, and L. Y. Yntema and L. F. Audrieth, from soln. of salts in formamide or acetamide, although H. Röhler obtained no deposit from soln. in formamide; and H. S. Booth and M. Merlub-Sobel obtained a deposit from a soln. of nickel thiocyanate in liquid ammonia.

According to G. Lambris,[4] some carbon may contaminate the deposit of nickel, and he concluded that the absorption of carbon is entirely due to a gas reaction, and that carbon dioxide or acetylene may introduce carbon into nickel or cobalt. Oxalic acid is partly reduced to acetylene on platinum and nickel, but not when copper, iron, or tin cathodes are employed. The carbon in electrolytic nickel is present in the form of a carbide. The subject was discussed by P. K. Frölich, and C. P. Madsen.

L. E. and V. E. Grant studied the variations in the thickness of electrodeposited nickel. W. Blum showed that the crystals of electrodeposited nickel decreased in

size as the current density increased up to 2 amps. per sq. dm.; the size of the crystals decreased with temp.; and with a decrease in the conc. of the metal ion. According to G. L. Clark and P. K. Frölich, a low current density, a low temp., and the presence of gelatin favour a fibrous or oriented structure—the evolution of hydrogen is unfavourable. The orientation of the structure is parallel to that of the cathode metal in the case of platinum. W. S. Barrows studied the effect of the nature of the anodes. The microstructure of the deposits was studied by R. Audubert, H. Stäger, W. D. Bancroft, G. Eger, A. K. Graham, A. N. Kuznetzoff and S. A. Baranoff, W. G. Burgess and W. Elenbaas, W. E. Hughes, G. L. Clark and P. K. Frölich, W. A. Wood, M. Z. Wolfmeyer, C. P. Madsen, C. Upthegrove and E. M. Baker, H. Kersten and J. Maas, V. Kohlschütter and co-workers, and B. Waser and E. H. Schultz. X-radiograms were observed by R. M. Bozorth, R. Glocker and E. Kaupp, J. D. Hanawalt and L. R. Ingersoll, H. Hirata and H. Komatsubara, and S. Procopiu. Most of the heavy metals—copper, silver, zinc, and lead—are normally deposited from simple acid soln. in a coarsely crystalline form, but with nickel, cobalt, and iron, under similar conditions, the metal is deposited in a finely crystalline form. Owing to its electropositive character, nickel is always deposited along with some hydrogen; this is not the case with copper, silver, or lead, and only to a small extent with zinc. Consequently, V. Kohlschütter suggested that the liberated hydrogen interferes with the growth of the crystals of nickel. S. Glasstone suggested that nickel is deposited in an unstable atomic form which is rapidly transformed into a more stable modification with the consequent interference of crystal growth. V. Kohlschütter and H. Schecht showed that the presence of colloidal metal hydroxides may have reduced the size of the crystals of electrodeposited nickel so as to produce a mirror-like surface; and H. J. S. Sand suggested that a similar effect may be produced by inorganic colloids in the course of electrolysis. According to J. B. O'Sullivan, the electrodeposits from buffered nickel sulphate soln. become smoother and more fine-grained as the P_H of the bath is raised so that neither the hypothesis of V. Kohlschütter nor that of S. Glasstone explains the results. He suggested that the effect is due to the presence of colloidal nickel hydroxide or basic salt in the cathode film. This is supported by the fact that electrodeposits contain a little oxygen. H. T. S. Britton found that nickel hydroxide is precipitated from nickel sulphate soln. when $P_H=6{\cdot}66$, and nickel borate probably behaves similarly; and D. J. MacNaughtan and A. W. Hothersall observed that on adding a soln. of sodium hydroxide to a nickel sulphate-boric acid plating bath, permanent precipitation begins when $P_H=6{\cdot}6$, but in an ammonium nickel sulphate bath it begins when $P_H=7{\cdot}6$. In general, J. B. O'Sullivan found that as the value of P_H is raised the deposits become smoother and finally more brittle—*vide supra*. J. B. O'Sullivan continues the discussion as follows:

According to P. K. Frölich, colloids affect the structure of an electrodeposit by forming a more viscous layer at or near the cathode, so that the diffusion thither of metal ions is hindered, and he visualized two ways in which this might take place. Firstly, the colloid may become pressed against the cathode owing to its particles carrying a positive charge. The metal ions will then have to pass through the channels of the sponge-like mass produced, and will be discharged immediately they reach the cathode surface, irrespective of the orientation of the metal atoms previously deposited. Thus the growth of existing crystals will be interfered with, and there will be a tendency for the metal to be deposited in needle-shaped crystals in the channels of the colloid mass until this becomes embedded in the metal deposit. If, however, the colloid is so firmly held against the cathode that this can take place, it is, to all intents and purposes, being electrolytically deposited with the metal. Also the quantity of colloid enclosed in the deposit would be so great as to constitute an extreme case, such as those described by W. D. Bancroft and T. R. Briggs, and by R. Marc, who obtained slimy deposits from solutions containing organic colloids. The latter describes his deposits as consisting of extremely thin

flakes, not needles, of metal, set in a collagenous mass. The other case suggested by P. K. Frölich is that in which the colloid has an amphoteric character, and the P_H of the cathode film is distinctly higher than that of the bulk of the solution. Such a case would be that of gelatine in a nickel or zinc plating bath. If the bath is sufficiently acid, the positively charged colloid will migrate towards the cathode, but at a definite distance from this it will encounter a region where the P_H is the same as its isoelectric point; beyond this region the P_H will be higher, so that the colloid would migrate away from the cathode. In the intermediate region, the colloid will be held, forming a diaphragm which will offer a resistance to the passage of metal ions, so that the colloid free liquid between this diaphragm and the cathode may become depleted of metal ions. But, according to W. E. Hughes, decreased concentration of metal ions in a simple solution results in slower deposition of metal, and consequently in the formation of a more coarse-grained, not a more fine-grained deposit. On the other hand, if there is produced at or near the cathode a viscous layer which is difficultly permeable to metal ions, the effect will be that the concentration of these in the cathode film will diminish, so that a greater number of hydrogen ions will be discharged, and the P_H of the cathode film will rise. Consequently, more colloidal metal hydroxide will be formed, and if it is produced in the cathode film more rapidly than it is being electrolytically deposited, the conditions will continue to be accentuated until all the available metal has been converted into hydroxide, whereafter this can only be replenished as more metal ions migrate or diffuse to the cathode film.

L. R. Ingersoll, F. Kirchner, and R. Glocker and E. Kaupp showed that the fibre axis represents the direction in which the velocity of deposition is a maximum. If the current density is too high, the crystals lose all regular orientation. R. M. Bozorth thought that the orientation of the crystals of iron, cobalt, nickel, during their electrodeposition is associated with strains. The subject was also studied by K. N. Oesterle. E. S. Hedges observed that a periodic electrodeposition could be obtained with a soln. of potassium nickel cyanide.

K. Okimoto [5] discussed the electric melting of nickel. As with iron (*q.v.*), L. Jordan and co-workers found that crucibles made from commercial, fused zirconia, magnesia, or alumina are not suitable for melting the purified metal; but crucibles made from the purified oxides gave good results. They preferred those made with purified magnesia. A. Dingwell and co-workers referred to the contamination of nickel by molybdenum when fused in a molybdenum resistance furnace.

G. Magnus [6] found that when the oxide is reduced at a low enough temp., **pyrophoric nickel** is formed, and W. N. Ipatéeff showed that in hydrogen the nickel is pyrophoric if reduced at temp. below 270°. G. Grassi obtained the pyrophoric metal by heating the oxalate or oxide in hydrogen at about 280°. According to H. Moissan, pyrophoric nickel is formed below 270° as a black powder which does not burn so brightly as iron reduced at 440° when it is exposed to air. If reduced at 270° to 280°, it is oxidized by dry air or oxygen only. G. Tammann and N. Nikitin discussed the effect of grain-size on the pyrophoric quality above 350°; moisture favours the oxidation so that in moist air or oxygen the powder is oxidized at a lower temp.

L. Graf [7] prepared single crystals of nickel. L. R. Ingersoll, and A. C. G. Beach prepared **nickel mirrors** and **nickel films** by spluttering nickel cathodes in hydrogen, nitrogen, and argon, or neon, with a direct current generator of 1000 volts, and allowing the metal to deposit on a cooled surface. These films, as well as films obtained electrolytically—*vide supra*—were studied by K. Lauch and W. Ruppert, J. Hanawalt and L. R. Ingersoll, L. R. Ingersoll and co-workers, R. M. Bozorth, K. M. Oesterle, O. G. Keiko, R. K. Cowsik, H. Bracchetti, F. Kirchner, F. H. Constable, C. Müller, J. Jolist, E. O. Hulburt, J. H. Howey, J. Strong and C. H. Cartwright, A. W. Gauger, R. Glocker and E. Kaupp, H. Hirata and H. Komatsubara, S. Procopiu, and V. Kohlschütter and co-workers—*vide* iron mirrors. F. W. Laird,

C. F. van Duin, and C. G. Fink and W. G. King found that by admitting nickel carbonyl vapour suddenly into an evacuated flask uniformly heated to 180° to 200° the walls may be coated with a bright, adherent, uniform deposit of nickel. The presence of traces of air, oxygen, chlorine, etc., is to be avoided because it leads to dark deposits. A preliminary flushing of the flask with hydrogen is effective in producing bright deposits, but is unnecessary if the vessel is evacuated to 5 to 10 microns press. Z. Debinska found that mirrors obtained by vacuum distillation exhibit orientation of the microcrystals. J. E. Henderson obtained a mirror of nickel by evaporating that metal from a heated tungsten filament. J. Manning prepared nickel membranes for ultra-filtration.

According to M. Kimura,[8] when metallic nickel is heated to incandescence and quickly plunged into distilled water, a **colloidal solution of nickel** and of nickel hydroxide is formed. G. Bredig did not have success in preparing the **hydrosol** by electrically spluttering the metal under water, but D. Zavrieff, A. H. Erdenbrecher, F. Ehrenhaft, J. Billitzer, E. Thorén, C. H. von Hoessle, T. Svedberg, O. Scarpa, and E. Thorén obtained the colloid in this manner. D. Zavrieff also prepared colloidal soln. by electric disintegration. C. Paal found that colloidal nickelous hydroxide is reduced to a colloidal soln. of nickel by hydrogen in the presence of a hydrosol of palladium. The stability of the colloid is increased if sodium protalbinate be present as protective colloid. The hydrosol so obtained is a brilliant chestnut-brown in transmitted light, and black in reflected light. The corresponding **hydrogel** forms blackish-brown, brittle lamillæ, and its state is reversible. L. Hogounenq and J. Loiseleur used glycogen as protective colloid. According to C. Kelber, a soln. of nickel formate and gelatine in glycerol at 200° to 210°, when submitted to the action of a stream of hydrogen, assumes a chestnut-brown colour. The colloidal soln. remains unaltered in the air and is miscible with alcohol, but on treatment with water and centrifuging, it deposits the colloidal metal as a dark brown solid, containing 25 to 30 per cent. of nickel, which can again yield colloidal nickel soln. in dilute acetic acid, acidified water, glycerol, or alcohol. Other reducing agents can be applied to the same purpose ; nickel formate at 220° in glycerol soln. in the presence of gelatine is reduced by hydrazine hydrate with formation of a colloidal nickel solution of similar properties to that just described. Formaldehyde, hydroxylamine, and hypophosphorous acid can also be applied as reducing agents for the purpose, whilst gum arabic can be used in place of gelatin. The nickel formate can be replaced by nickel acetate or freshly-precipitated nickel hydroxide. B. C. Soyenkoff prepared colloidal nickel soaps. H. Freundlich and W. Seifriz studied the electric charge of the colloid. According to Wo. Ostwald, when a soln. of nickel carbonyl in benzene is boiled, carbon monoxide is evolved, and a violet-grey **organosol,** or **benzenosol,** of nickel remains. T. Svedberg obtained an **alcoholsol** by the electrical spluttering of nickel in *iso*butyl and other alcohols, and an **ethersol** using ethyl ether as the dispersion medium ; S. R. Rao, and C. G. Montgomery, with *iso*propyl alcohol ; and S. J. Folley and D. C. Henry, an **acetonesol,** where traces of water reduce the stability of the sol, and traces of sulphuric, hydrochloric, or *m*-hydroxybenzoic acid, or *m*-nitroaniline, make the sol more stable. E. Hatshek and P. C. L. Thorne obtained sols by dissociating nickel carbonyl in benzene, toluene, and *para*cymene with rubber as protective colloid ; and F. Haurowitz obtained a stable sol of nickel in benzene. H. B. Weiser and G. L. Mach discussed the subject. W. E. Gibbs and H. Liander prepared **aerosols** of nickel.

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§ 5. Nickel as a Catalyst

Numerous examples of the work of nickel as a catalyst are indicated in connection with the chemical properties of nickel. Nickel intended for use as a catalytic agent is usually prepared by reducing the green hydroxide with hydrogen at a temp. below 300° ; if the metal be reduced at a higher temp. than this, it is less reactive ; and if it be reduced at a bright red heat, the nickel is almost inert. The presence of halogens, arsenides, phosphides, or sulphides, poisons the catalyst, *i.e.* these agents reduce the activity of the catalyst. Consequently, as emphasized by P. Sabatier and J. B. Senderens,[1] and A. W. Crossley, it is necessary to employ purified hydrogen for hydrogenation reactions with nickel as catalyst. T. Kusama and Y. Uno discussed why the catalyst prepared from nickel chloride is less active than when it is prepared from the nitrate, and they concluded that it was due to the presence of unreduced chlorides. The poisoning of the nickel catalyst was studied by B. Kubota and K. Yoshikawa, F. Wolff, K. Yoshikawa, M. C. Boswell and C. H. Bayley, and G. Roberti.

In some cases, C. Kelber found it better to scatter, say, the carbonate, over some inert material like asbestos, kieselguhr, or animal charcoal, and then reduce the carbonate. Nickel reduced from the carbonate at 450° has no action on a mixture of hydrogen and oxygen at ordinary temp., but if the nickel be spread over an inert substance, its activity is augmented. It is still more active if reduced at 300°. W. E. Gibbs and H. Liander reduced the nickel from the carbonyl, and observed that it has but little catalytic effect on the reduction of carbon monoxide, or of ethylene by hydrogen. K. Schirmacher and co-workers associated the catalyst with silica gel ; and P. Breteau obtained finely-divided nickel by reducing a hot soln. of nickel sulphate with sodium hypophosphite. L. R. Ingersoll examined the catalytic effect of films of nickel spluttered in nitrogen. According to E. Maschkilleisohn, nickel has an optimum degree of dispersion for use as a catalyst, any finer dispersion is accompanied by a reduction, and finally by a cessation of its activity. The subject was studied by A. A. Balandin, L. H. Reyerson, E. Biesalsky and co-workers, A. Brochet, C. F. Fryling, C. R. Glass and L. Kahlenberg, K. Heinze, S. Iki, T. Kusama and Y. Uno, M. Lietz, C. M. Loane, E. J. Lush, E. Maschkilleisohn, W. Normann, J. E. Nyrop, K. Omiya, A. Quartaroli, B. Kubota, M. Raney, K. Schirmacher and co-workers, A. Svizuin, R. Thomas, F. Thorén, and E. Wolfson. G. M. Schwab and L. Rudolph, and H. N. Huntzicker and L. Kahlenberg, discussed the nature of the catalyst ; G. Bredig and R. Allolio, the X-ray properties of the

catalyst; H. L. Waterman and M. J. van Tussenbroek, and H. Adkins and L. W. Covert, the mode of preparation of the catalyst; F. Fischer and K. Meyer, the reduction temp.; G. M. Schwab and H. Schultes, and F. H. Constable, the surface area; A. Bag, the re-activation of nickel; A. W. Gauger and H. S. Taylor, the effect of various supports for the catalyst; T. Kusama and Y. Uno, the effect of chlorine; W. W. Russell and H. S. Taylor, the effect of thoria. C. Kelber studied the effect of water; F. Wolff, the effect of ferric and nickel hydroxides; and G. F. Schoorel and co-workers, the effect of high pressures on the hydrogenation. O. Schmidt compared the hydrides of the metal.

E. Bosshard and E. Fischli,[2] W. Norman, W. Norman and W. Pungs, W. Meigen, and W. Meigen and G. Bartels favour the opinion that it is not nickel oxide, but rather the free unoxidized metal which behaves catalytically. F. Bedford and E. Erdmann, J. B. Senderens and J. Aboulenc, and W. Siegmund and W. Suida consider that no reduction of nickel oxide to the metal occurs during hydrogenation; and they suggested that possibly the suboxide, Ni_2O, described by I. Bellucci and R. M. Corelli, is formed. The hydrogen transfer takes place *viâ* an intermediate phase represented by:

$$\begin{matrix} H\,\vdots\,C{-}Ni \\ H\,\vdots\,C{-}Ni \end{matrix}\!>\!O \qquad \text{or by} \qquad \begin{matrix} H.Ni \\ H.Ni \end{matrix}\!>\!O$$

It is also possible that the transfer takes place through the decomposition of water, forming nascent hydrogen: $Ni_2O+H_2O=2NiO+2H$, which then unites with the compound being reduced whilst the nickel monoxide is again reduced to the suboxide by the hydrogen. G. Bartel's experiments on the speeds of the reaction with nickel and with the alleged suboxide did not support this hypothesis, nor did W. N. Ipatéeff's experiments on the reduction of benzene. The subject was discussed by C. Kelber, and M. C. Boswell.

Another hypothesis is that the hydrogen is activated by passage into the atomic state, by occlusion or adsorption by the nickel—*vide supra*, the action of hydrogen on nickel. Yet a third hypothesis assumes that the hydrogen and the compound to be reduced mutually form a kind of surface film on the nickel, and that the juxtaposition enables the molecular hydrogen to do work that it could not perform by simple contact. The subject was discussed by M. Polyakoff, and R. Foresti.

B. S. Srikantan discussed the relation between the atomic energy and the efficiency of nickel as a catalyst; C. F. Fryling, R. Kuhn, O. Schmidt, H. P. Cady and W. E. White, and A. A. Balandin, the mechanism of reductions with nickel as catalyst; and B. Kubota and K. Yoshikawa, the formation of the metal hydride in hydrogenations with nickel as catalyst. G. L. Clark and co-workers showed that differences in the activities of nickel catalysts are not due to differences in the type or dimensions of the lattice.

According to H. S. Taylor, X-radiograms show that metallic catalysts possess the definite lattice structure of the crystalline material, and there are, on the surface, groups of atoms in which the crystallization process is incomplete. The surface is to be regarded as composed of atoms in varied degrees of saturation by neighbouring metal atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint only, and it is by this constraint alone that these outermost atoms differ from gaseous metal atoms. These atoms can attach to themselves or adsorb three molecules, the linking between which and the nickel atom is identical with that obtaining in nickel carbonyl. This concept introduces a mechanism whereby both constituents of a hydrogenation process may be attached to one nickel atom and obviates the necessity, inherent in the Langmuir scheme, of having both reactants adsorbed on adjacent elementary spaces. The idea of metallic atoms detached to varying extents from the normal crystal lattice is in harmony with observations on such catalytic surfaces. According to E. F. Armstrong and T. P. Hilditch, the attraction between the unsaturated organic molecule and unsaturated nickel atom is held to be strong enough to loosen

the nickel atom from its adjacent atom or atoms, so that when catalytic change actually occurs the nickel atom loses all contact with its neighbours. For the moment, there may exist, actually apart from the solid surface, a combination of nickel, unsaturated compound, and probably hydrogen as well. F. P. Bowden and E. K. Rideal studied the effect of cold-work and annealing on the areas of catalytic activity.

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§ 6. The Physical Properties of Nickel

The **colour** of nickel is silver-white with a grey tinge, and, when electrodeposited, the metal may be bright and lustrous, or, as pointed out by J. M. Merrick,[1] dark and matte. Nickel can take a high polish so that it reflects a large proportion of the light falling on a polished surface. This makes the metal valuable for electroplating. A. W. Wright found that thin films of nickel viewed in transmitted light appear grey or brownish-grey; and G. T. Beilby said olive-green, or blue. W. L. Dudley observed that the incandescent vapour appears bluish-green. E. van Aubel discussed the colour and transparency of nickel. W. T. Brandt compared the decolorizing power of nickel, zinc, and tin on copper:

Copper (per cent.)	Cu–Ni Alloy	Cu–Sn Alloy	Cu–Zn Alloy
95	Paler than copper	Red (golden) yellow	Almost copper-red
90	Light copper-red	Reddish-grey-yellow	Yellowish-reddish
85	Pale red	Reddish-yellow	Reddish-yellow
80	White pink tinge	Reddish-grey	Reddish-yellow
78	Nearly white	Yellowish-grey	Reddish-yellow
75	Nearly white	Reddish-white	Pale yellow
70	Silver-white	White	Yellow

G. Rose observed that the crystalline fracture shows that the **crystals** belong to the cubic system, though S. Kalischer was unable to establish this by **corrosion figures.** R. M. Bozorth and F. E. Haworth, and H. H. Potter and W. Sucksmith studied the corrosion figures. G. J. Sizoo, and C. H. Mathewson discussed the **twinning** of the crystals; and A. Schrader and E. Weiss observed no twinning of the crystals, nor did they find any twinning or grain-growth develop during annealing. F. C. Thompson and W. E. W. Millington, and J. A. Ewing and W. Rosenhain observed **slip-bands** and twinning lamellæ in nickel. A. Schrader and E. Weiss studied the twinning of nickel. G. T. Beilby observed that the polished metal has a transparent glass-like skin which may pass into minute scales or granules. W. G. Burgers and W. Elęnbaas studied the zone-like structure of electrolytic nickel. The **microstructure** after etching the polished surface is fairly typical of polycrystalline metals. E. S. Davenport discussed the sub-crystalline boundaries. The microstructure of nickel was studied by W. Velguth, and R. Vogel. According to P. D. Merica and R. G. Waltenberg, nickel oxide or sulphide, and manganese sulphide are sometimes visible; if over 0·4 per cent. of carbon is present, it usually occurs as graphite. The intercrystalline brittleness was shown by H. S. Rawdon and co-workers to be due to the oxidation or sulphurization of the grains so that their cohesion is destroyed. G. Tammann studied the effect of annealing on the adsorption of dyes by nickel wires; and G. Tammann and A. Rühenbeck, the welding power of nickel. H. C. H. Carpenter examined the effect of the imprisoned gas.

The etching of the metal was studied by J. Czochralsky, and H. S. Rawdon and co-workers. According to W. A. Mudge, the microstructure can be developed by etching with 5 to 100 per cent. nitric acid—say, by diluting a soln. of the 50 to 75 per cent. acid with commercial 50 per cent. acetic acid. H. S. Rawdon and M. G. Lorentz recommended conc. hydrochloric acid; or a soln. of ferric chloride acidified with hydrochloric acid; and for electrolytic etching, a current density of 0·01 amp. per sq. cm. and an electrolyte of sulphuric acid, 22 parts by vol., 3 per cent. hydrogen dioxide, 12 parts by vol., and 66 per cent. of water by vol.; or else, as electrolyte, a 5 per cent. soln. of a mixture of nitric and sulphuric acids, 3 : 1.

A. H. Hull reported that the **X-radiograms** of nickel correspond with both a face-centred and a body-centred cubic lattice, and that the lattice constant length of edge of cube of the face-centred form is a=3·54 A. F. Wever found no evidence of the existence at ordinary temp. of two forms of nickel with different space-lattices. The atomic arrangement is uniformly that of a body-centred, cubic lattice with a parameter $a=519\times10^{-8}$ cm. Impurities may increase the distances

between the atoms. Non-magnetic or β-nickel, like β-iron, cannot be regarded as an allotropic form with a lattice structure different from that of ordinary or α-nickel. S. B. Hendricks and co-workers could detect no evidence of any allotropic change in nickel up to 1015°, and the body-centred form has not been detected by other observers, but the lattice constant of the face-centred form was found by W. P. Davey, and G. L. Clark and co-workers, to be 3·499 A.; F. Wever, and L. W. McKeehan, 3·51 A.; H. Lange, 3·518 A.; A. Osawa, 3·508 A.; L. Mazza and A. G. Nasini, 3·514 A.; S. Holgerson, 3·52 A.; H. Bohlin, and L. Vegard and H. Dale, 3·53 A.; A. Westgren and A. Almin, 3·519 A.; W. C. Phebus and F. C. Blake, 3·521 A.; Z. Jeffries and R. S. Archer, E. C. Bain, A. W. Hull, R. W. G. Wyckoff, and A. Sacklowsky, 3·54 A.; R. G. Kennedy, 3·525 A. for 99·94 per cent. nickel; F. Wever, 3·51 A.; L. W. McKeehan, 3·510 A.; and E. A. Owen and J. Iball gave a=3·5179 A.; and they calculated the closest approach of the atoms to be 2·487 A. The subject was discussed by R. Brill and H. Pelzer, M. I. Gen and co-workers, A. O. Jung, E. Piwowarsky, R. Riedmiller, P. Röntgen and W. Koch, J. E. L. Jones and B. M. Dent, W. Büssem and F. Gross, H. Karlsson, E. A. Owen and E. L. Yates, H. Kersten and J. Maas, K. Becker, E. R. Jette and F. Foote, and E. C. Bain. G. L. Clark and co-workers observed that nickel catalysts prepared in different ways, and with different activities, all gave identical lattices with a=3·536 A. W. P. Jesse found the length of the edge of the cubic lattice of nickel at:

	20°	900°	1000°	1100°	1200°
a A. . . .	3·518	3·568	3·575	3·583	3·592

L. Mazza and A. G. Nasini, G. Hägg and G. Funke, H. Bohlin, R. M. Bozorth, N. Uspensky and S. Konobejewsky found that nickel obtained by electrodeposition, by the decomposition of nickel carbonyl, and by the reduction of the oxide, crystallizes in face-centred cubes. The dimensions of the crystal particles are 10^{-2} to 10^{-5} cm. The length of the elementary cell is 3·514 A. L. H. Germer said that with single crystals of nickel, the X-radiograms show patterns due (i) to the face-centred cubic space-lattice of the crystal; (ii) the first or outermost layer of nickel atoms; (iii) a monatomic layer of adsorbed gas; and (iv) an outer thicker layer of absorbed gas. S. Dembinska, and W. Büssem and F. Gross studied the crystal structure of thin films. W. Hume-Rothery studied the relations amongst the lattice constants of nickel, and other elements.

G. Greenwood discussed the fibrous texture of nickel wires. The unit face-centred, cubic lattice of cold-drawn nickel wire has the edge a=3·515 A.; and the crystals are arranged so that the (111) and (100)-faces are parallel with the axes of the fibres. G. Tammann found that in rolling nickel, the icositetrahedral and octahedral planes tend to form parallel to the surface. W. A. Wood studied the distortion of the lattice with electrodeposited nickel; C. B. Hollabaugh and W. P. Davey, the orientation of the crystals by cold-rolling; S. T. Konobejewsky, and E. van Aubel studied the distortion of the space-lattice by mechanical work; and F. von Göler and G. Sachs, F. Krau, G. Tammann and co-workers, W. A. Wood, E. Schmid, M. Bonzel, G. W. Brindley and F. W. Skiers, W. E. Schmid and E. A. W. Müller, S. T. Konobejewsky, and C. B. Hollabaugh and W. P. Davey, the effect of cold-rolling on the lattice structure.

Pure, cold-drawn nickel, after various heat-treatments, although sometimes showing peculiar re-crystallization effects, always crystallizes in face-centred, cubic crystals; the re-crystallization cannot be detected by X-ray analysis for temp. up to 940°; the appearance of characteristic re-crystallization structures is observed only when the metal has been annealed at temp. upwards of 1000°. A prolonged annealing at 1200° for 30 hrs. produces coarse grains, irregularly oriented, giving rise to a marked reduction of ductibility and tensile strength. Quenching does not produce any change in the lattice structure. H. Schottky and H. Jungbluth said that the first signs of re-crystallization occur at 500°; and G. Wazau, and

Z. Jeffries and R. S. Archer gave 600° for the temp. of re-crystallization, and the theory of the subject was studied by J. A. M. van Liempt. F. Sauerwald discussed the grain-growth of nickel during sintering. G. Tammann and W. Salge gave 200° to 220° for the beginning of re-crystallization.

G. Bredig and R. Allolio said that some samples of electrolytic nickel deposited in an atm. of hydrogen at a few tenths of a mm. press., seemed to have a close-packed, hexagonal structure when that of electrodeposited nickel is a typical face-centred cube, with $a=3{\cdot}514$ A. According to G. Wazau, the structure of electrolytic metal usually consists of parallel lines of crystals packed in layers parallel to the surface of the cathode. After annealing at 600°, in the absence of air, the metal shows signs of re-crystallization characterized by a widening of the lines, and their separation into elongated crystals. After annealing at 900°, the re-crystallization is complete, and the new crystals are the smaller the greater is the press. to which the metal has been previously subjected. The hardness rapidly falls on the annealing temp. changes from 500° to 700°, and it thereafter falls more slowly. Annealing does not reduce the brittleness due to occluded hydrogen. The orientation of the electrodeposited crystals was studied by G. L. Clark and P. K. Frölich, C. Upthegrove and E. M. Baker, G. W. C. Kaye, R. Glocker and E. Kaupp, A. K. Graham, R. M. Bozorth, D. J. Macnaughtan and co-workers, and G. E. Gardam and D. J. Macnaughtan.

L. R. Ingersoll and J. D. Hanawalt found that the film of nickel formed by spluttering the metal in hydrogen is non-magnetic, and it is initially amorphous, or else the crystals are too small to detect. It then crystallizes with a lattice like that of the massive metal, or else the lattice may be more or less distended. The distorted lattice is face-centred and cubic, being about 6 per cent. larger than that of ordinary nickel. If the film be de-gassed by heating it to about 400°, normal crystals are formed. If the nickel be spluttered in nitrogen, a non-magnetic, metallic film is produced, and it has a face-centred, tetragonal lattice with $a=3{\cdot}994$ A., and $c=3{\cdot}760$ A., so that the axial ratio $a:c$ is $1:0{\cdot}92$. Nickel *en masse* has a face-centred, cubic lattice with $a=3{\cdot}517$ A. W. P. Jesse observed no new form of nickel between 450° and 1200°. S. Valentiner and G. Becker observed a normal, face-centred, cubic lattice, with edge $a=3{\cdot}51$ A., in all nickel films obtained by spluttering in hydrogen. G. P. Thomson said that films of nickel deposited by spluttering on rock-salt, in an atm. of argon, exhibit a hexagonal structure with a lattice having $a=4{\cdot}06$ A., and $c=8{\cdot}86$ A. This result is different from that observed by G. Bredig and R. Allolio, but G. Bredig and E. Schwarz von Bergkampf found that nickel spluttered from a cathode hydrogen gives a non-magnetic mirror of the metal with a hexagonal lattice, and that if the mirror be heated in hydrogen, the metal then has the ordinary cubic lattice. E. Rupp examined the effect of adsorbed hydrogen on the space-lattice; and O. Werner, the diffusion of radium emanation. V. Kohlschütter and co-workers, M. I. Gen and co-workers, G. D. Preston, M. Miwa, W. Büssem and F. Gross, and S. Dembinska studied the crystal structure of thin films; and H. Reininger, the structure of sprayed films.

The **specific gravity** of nickel given by the early observers was determined on more or less impure samples. The reduced nickel may also appear as a more or less compact sponge with numerous voids or pores, and hence A. K. Huntington and W. G. McMillan [2] stated that the data may often be misleading. T. Bergman reported 9·00. R. Tupputi gave for the metal which had been reduced from the oxide by carbon and then melted, 8·38 at 12·5°; R. J. Haüy, and H. Schröder gave 8·9. The metal reduced by carbon monoxide was found by J. B. Richter to have a sp. gr. of 8·279; and C. D. Tourte gave 8·402 at 12·5°; whilst for the metal reduced by hydrogen, C. F. Rammelsberg gave 8·975 to 9·261; S. Bottone, 8·279 at 15·5°; and L. Playfair and J. P. Joule, 7·803 to 7·861. C. Brunner found 8·637; M. J. Brisson, 7·807; A. Arndtsen, 8·88 at 4°; L. Thompson, 8·575; C. H. Lees, 8·80 for 99 per cent. nickel; D. F. McFarland and O. E. Harder, 8·69; R. Böttger,

8·477 to 8·713; W. F. Barrett, 8·3; H. Tomlinson, 8·707 for hard-drawn, and 8·739 for annealed nickel wire; L. Thompson, 8·575 for the purified metal; C. Winkler, 7·5185 at 20°; O. Bloch, and W. A. Tilden, 8·790 at 21°/4°; and R. von Dallwitz-Wegner, 8·90; W. von Selve, 8·6 to 8·9 for the rolled metal; P. D. Merica, 8·70 to 8·90 for malleable or electrolytic nickel, and 7·7 to 8·0 for spongy nickel or nickel powder. J. A. Fleming found the sp. gr. of annealed electrolytic nickel to be 8·96 at 18°. L. Mond and co-workers found that nickel powder reduced by hydrogen from nickel oxide obtained from nickel deposited by the carbonyl process, has a sp. gr. 8·2834 at 15·4°, and 8·2928 at 15·1°. D. H. Browne and J. F. Thompson found samples of commercial nickel with a sp. gr. ranging from 7·993 to 8·873; and samples of malleable nickel ranging from 8·71 to 8·90—average, 8·84. P. D. Merica and co-workers gave 8·85±0·03 for the sp. gr. of commercial, 99·2 per cent. nickel. H. Copaux gave 8·8 for the metal at 15°/4°, and this may be taken to be the best representative value. R. Tupputi gave 8·820 for the sp. gr. of the rolled metal, at 12·5°, and 8·380 for the cast metal; analogous results—respectively 8·666 and 8·279—were obtained by J. B. Richter; respectively, 8·932 and 8·402, by C. D. Tourte; respectively, 8·8404 and 8·8209, by W. Schlett; respectively, 8·9 and 8·85, by M. Maclean; and, respectively, 8·8 and 8·3, at 15°/4°, by H. Copaux. G. W. A. Kahlbaum and E. Sturm found that the cold-drawn wire had, at 20°/4°, a sp. gr. 8·7599, and when annealed, 8·8439; similarly, with wire twisted in the cold, the sp. gr. was 8·8273, and when annealed, 8·8412; T. Ueda also studied the effects of torsion. T. M. Lowry and R. G. Parker gave 8·8583 for the metal in bulk and 8·8299 for the cold-worked metal (filings). E. L. Peffer found the sp. gr. of cast nickel—99·94 per cent. Ni—to be 8·907 at 23°; that of a cold swaged rod 0·225 in. diam., 8·901 at 25°; and that of the annealed rod, 8·902 at 25°. A coarsely crystalline ingot which had received no mechanical work had a sp. gr. 8·907, and when reduced by cold-work, either annealed or not annealed, 8·90. The results were discussed by F. C. A. H. Lantsberry, and C. B. Hollabaugh and W. P. Davey. R. G. Kennedy calculated from the lattice parameters the sp. gr. 8·917; G. L. Clark, 9·1; Z. Jeffries and R. S. Archer, 8·8; and L. W. McKeehan, 8·953. R. A. Hadfield gave 8·839 for ordinary cast nickel and 8·826 for forged nickel. S. Kaya found the sp. gr. of single crystals exceeded that of the polycrystals by 0·110 per cent. K. Honda and co-workers gave 2·06 per cent. for the expansion which occurs with the solidification of nickel with 2·2 per cent. of carbon. C. Benedicks and co-workers found the **specific volume** of nickel is 0·1258 at 1422°, and 0·1288 at 1500°; and J. A. Groshans, and E. Donath and J. Mayrhofer made observations on the sp. vol. of nickel; and T. W. Richards gave 6·7 for the **atomic volume.** W. Biltz and K. Meisel calculated 557·26 for the at. vol. at absolute zero. W. L. Bragg gave for the **atomic radius** 1·35 A. G. Natta and L. Passerini found that if the at. radius of oxygen is 1·32 A., that of nickel is 0·77 A. Observations were made by A. Kapustinsky, A. Ferrari and F. Giorgi, V. M. Goldschmidt, E. H. Westling, H. G. Grimm, J. C. Slater, E. Herlinger, E. J. Cuy, G. Natta and L. Passerini, W. P. Davey, L. Pauling, and E. T. Wherry, from which it follows that for tervalent nickel atoms, the effective radius is 0·35 A.; for bivalent atoms, 0·69 to 0·78; and for neutral atoms, 1·24 to 1·39 A. M. L. Huggins gave 1·59 to 1·77; A. Kapustinsky studied the effect of solvation on the ionic radius. J. A. M. van Liempt discussed the atomic constants of nickel; and P. Vinassa, the molecular number.

J. B. Dumas observed that the **hardness** of nickel is such that it is scratched by glass of hardness 2·6 on Mohs' scale; S. Bottone gave for the cutting hardness 1410 when that of cobalt is 1450, iron, 1375, and copper, 1360; H. Copaux found a hardness of 3·5 on Mohs' scale; and T. Turner reported the hardness of nickel to be 1410 when that of cobalt is 1450; that of copper, 1360; that of the diamond, 3010; and that of iron is 1375. L. Thompson stated that the purified metal which he prepared was as soft as copper. F. Robin found the penetrative hardness of nickel to be 105 to 190, and, when annealed, 130 to 150. The value for copper is 52 to 54. M. Waehlert gave 56 for the Brinell's hardness of nickel; C. A. Edwards,

144·0; and A. Krupkowsky, 59·1. W. B. Price and P. Davidson obtained for Brinell's hardness of bars which had been cold-rolled from 0·5 in. to 0·134 in.:

	As rolled	Annealed at			
		250°	350°	450°	550°
Hardness	235	262	255	248	228

L. Jordan and W. H. Swanger gave for the scleroscope hardness of 99·94 per cent. nickel, 5·0; for the Rockwell hardness, 42 to 44; and for Brinell's hardness, 68 to 78. They also found for cold-worked, and nickel annealed 30 min. at different temp.:

	Cold-worked	Annealed for 30 min.			
		650°	750°	850°	950°
Rockwell . . .	63–68	52–59	51–59	35–52	15–18
Scleroscope . .	12–19	8–13	8–13	7–11	4–6

The results of F. Sauerwald and co-workers on the impact hardness of nickel are summarized in Fig. 2. Measurements were also made by H. Pécheux, T. Kawai, W. A. Mudge and L. W. Luff. D. J. MacNaughtan and A. W. Hothersall found the Brinell's hardness of electrodeposited nickel is increased from 162 to 250 by additions of sodium sulphate, and the substitution of potassium chloride by sodium fluoride in the bath of nickel sulphate, boric acid, and potassium chloride. M. Guichard and co-workers found the hardness of electrodeposits to vary from 155 to 420; D. J. MacNaughtan studied the porosity of the deposits. F. Sauerwald observed that the drop hardness decreased slowly between 20° and 300°, then more rapidly between 300° and 400°, increased slightly at 450°, decreased rapidly between 600° and 700°, increased slightly at 800°, and then decreased on to 914°. The decrease between 300° and 400° is attributed to the magnetic transformation; and the maximum at 450° is ascribed to *blue-brittleness* similar to that of iron. L. Guillet, and J. Cournot and S. Silva measured the hardness and fragility of nickel at temp. ranging from 20° to −190°. T. K. Rose found that the metal hardened by cold-work is softened by annealing between 530° and 700°. Measurements were also made by A. Kurth. According to K. Ito, the Brinell's hardness, H, of nickel is:

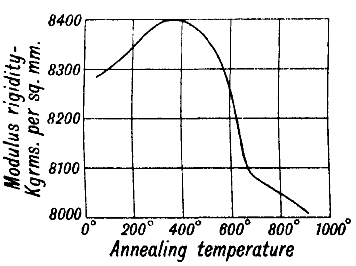


FIG. 2.—Brinell's Hardness of Nickel annealed at Different Temperatures.

	−43°	−18°	0°	35°	51°	65°	82°	109°	125°	148°
H . .	91·5	89·4	89·0	87·4	86·6	87·0	86·6	86·0	84·8	84·0

and the relation can be represented by $\log H_2 - \log H_1 = \alpha(2-1)$, where the temp. coeff. $\alpha = 0·00015$. The temp. coeff. of the hardness α and the m.p. T_m on the absolute scale of a number of metals are related by $T_m(\alpha + 0·00145) = 2·5$—*vide* iron. F. Sauerwald and E. Jänichen studied the adhesion of the compressed powder. O. Schwarz found for the percentage reduction by rolling, the Brinell's hardness:

Reduction .	0	6·0	9·1	20·8	39·5	60·2	80·0	88·0 per cent.
Hardness .	42·0	102·8	116·0	156·1	192·8	216·0	231·2	236·0

Observations were also made by G. Tammann, B. Bogitch, F. Sauerwald and K. Knehans, F. Krau, H. Schottky and H. Jungbluth, H. O'Neill, G. Wazau, H. J. Tapsell and J. Bradley, F. P. Romanoff, M. Guichard and co-workers, G. Kroll, and W. Kroll. D. H. Browne and J. F. Thompson found that the effects of varying physical and chemical conditions on the Brinnell's and Shore's hardness

of nickel are shown by the following tests for nickel bars hot-rolled, and afterwards cold-rolled to the reduction stated:

	0·06 per cent. C.		0·08 per cent. C.		0·09 per cent. C.		0·26 per cent. C.	
	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore
Hot-rolled	99	13	103	15	112	13	137	14
Reduction by cold rolling 25 per cent.	170	28	170	28	187	28	241	34
50 ,,	196	28	212	29	217	33	293	39
66 ,,	217	33	217	33	235	35	302	44
75 ,,	228	35	223	35	235	35	332	40
Annealed at 900°	89	9	92	9	92	9	99	11

D. H. Browne and J. F. Thompson found for the Brinell's hardness of nickel with different proportions of carbon:

Carbon	0·06	0·08	0·09	0·26 per cent.
Annealed at 900°	89	92	92	99
Hot-rolled—75 per cent. reduction	99	103	112	137
Cold-rolled—75 per cent. reduction	228	223	235	332

A. Mallock found the **velocity of sound** in nickel to be 4973·4 metres per second. G. W. Pierce studied the subject. J. Kleiber found that the velocity of sound in metals is proportional to the sq. root of the product of the sp. ht. and the linear coeff. of expansion. W. F. Barrett found that the conductivity of nickel for sound is 14·9 when that of air is unity. F. Robin studied the **acoustic properties,** and found that purified nickel exhibits little resonance. T. Gnesotto and L. A. Alberti observed breaks in the viscosity and rigidity curves of nickel at the Curie point. The curve, Fig. 3, for forgeable annealed nickel shows that the duration of sound diminishes as the temp. rises to about 60°, after which the curve remains horizontal or falls very slowly up to about 150°. The resonance falls again up to 300°, after which, under the influence of the allotropic change, β-nickel, it rises up to 340°, subsequently falling again once for all, until, on reaching a red-heat, the sound is extinguished. The curves for stressed and annealed nickel are also shown in Fig. 3. Ordinary and somewhat impure nickel possesses fairly considerable resonance. As the result of interstrain the peculiarity exhibited in the curve at about 150° disappears, and the sinuosity of the curve at the peculiar point just noted is greatly diminished. Annealing restores to the metal its original properties, and the curve of the duration of the sound becomes parallel with that of pure annealed nickel.

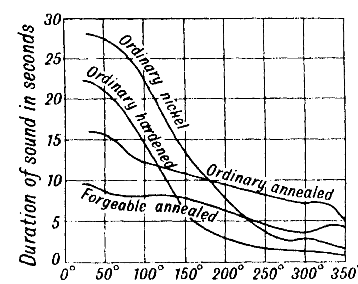


Fig. 3.—The Acoustic Properties of Nickel.

Some of the **mechanical properties** of nickel were noted by the early workers. J. B. Richter [3] observed that nickel is hard and susceptible of a high polish, it is very ductile, and may be hammered, either hot or cold, into plates $\frac{1}{100}$th in. thick, or drawn into wires $\frac{1}{54}$th in. in diam. In more recent times it has been rolled into sheets 0·0008 in. in thickness, and drawn into wires of 0·0004 in. in diam. O. W. Ellis studied the malleability. According to L. Thompson, the malleability of purified nickel is so great that it can be rolled out nearly to the thickness of tin-foil. R. Tupputi said that nickel wears down a file rapidly, and when bent, it becomes hot, and shows an indented fracture. Its malleability is diminished by dissolved carbon or manganese. C. Brunner, and O. L. Erdmann emphasized the brittleness of the nickel which they prepared, and added that when broken by repeated hammering it may exhibit a lustrous, coarse-grained fracture. H. St. C. Deville showed that the metal can be forged without undue oxidation, and the wires are nearly 15 times as tough as iron wires of equal thickness.

T. Fleitmann found that additions of zinc or magnesium augment the toughness and malleability of nickel, and several other metals—Cd, Sn, Pb, Mn, and Fe—can be alloyed with nickel without impairing its working properties. W. C. Roberts-Austen added that the effect of 0·001 part of magnesium is marked. H. Wedding observed that manganese favoured the tensile properties of nickel; and J. Garnier found that 0·003 part of phosphorus enhances the working properties of nickel. H. Wedding, and G. von Selve and F. Lotter added that the cracking and poor working properties of some varieties of nickel are due to the presence of oxygen as nickelous oxide, and this can be overcome by adding deoxidizing agents—*e.g.*, manganese, magnesium, etc.—to the molten metal.

Commercial nickel is not always malleable, and this is satisfactory when the metal is required for making alloys, but for making rods, wires, sheets, etc., malleability is an essential quality. If the metal be cast without magnesium, it is weak, and not malleable hot or cold, and a section of the casting is often honeycombed with blow-holes; cast with the magnesium—malleable nickel, previously described—the nickel is sound, homogeneous, and strong; it can be worked hot or cold; and in this malleable state it can be forged, rolled, cast, drawn into wire, spun, and otherwise worked. D. H. Browne and J. F. Thompson recommended 1200° for hot-rolling, and added that a temp. much in excess of this produces a condition approaching red-shortness; and that annealing begins at about 750°, full softness being attained at 900°—the temp. recommended for annealing. G. E. Gardam and D. J. MacNaughtan found that annealing electrodeposited nickel reduces the tensile strength.

According to J. B. Richter, and L. Thompson, nickel can be welded like iron, but C. D. Tourte succeeded in **welding** the metal only imperfectly. D. H. Browne and J. F. Thompson observed that nickel cannot be welded in the ordinary sense, *viz.* heating in a blacksmith's forge and hammering to a solid weld as with wrought iron. This is due to the absence of a proper flux to dissolve and remove the nickel oxide produced by heating. If the operation be conducted in a reducing atmosphere, nickel readily welds. Nickel can also be welded by means of the oxyacetylene flame, by electric spot-welding, or by butt-welding, where the two pieces form the electrodes and are pushed together so as to extrude the oxide from the weld. In this way it is possible to weld nickel wire to iron to form tips or points for spark-plugs, etc. F. Sauerwald and E. Jaenichen studied the adhesion between surfaces of the metal.

M. F. Angell found that the elasticity of nickel is greatly reduced by quenching, but it can be increased to its original value by annealing at a high temp. The **elastic modulus,** or **Young's modulus,** was found by M. Cantone to be 22,790 kgrms. per sq. mm.; G. S. Meyer gave 21,680 kgrms. per sq. mm.; H. J. Tapsell and J. Bradley, E. Grüneisen, O. Faust and G. Tammann, J. Galibourg, A. Wassmuth, K. F. Slotte, and W. Meissner, 20,000 to 22,000 kgms. per sq. mm.; and W. Voigt, 20,300 kgrms. per sq. mm. G. Searle gave 23,950 kgrms. per sq. mm. for the drawn metal, and C. Schaefer, 23,544 kgrms. per sq. mm. W. Sutherland noted that the recorded results gave the average value 22,400 kgrms. per sq. mm. H. Tomlinson gave 2271×10^6 grms. per sq. cm. for hard-drawn wire, and 2175×10^6 grms. per sq. cm. for annealed wire. A. L. Kimball and D. E. Lovell gave 21×10^{11} dynes per sq. cm. for the cold-rolled metal; and K. Honda and T. Tanaka, $1{\cdot}930\times10^{12}$ dynes per sq. cm. D. K. Froman's results for Young's modulus with small stresses are summarized in Fig. 4. L. C. Tyte observed that nickel, like other metals examined, shows a deviation from Hooke's law over the whole experimental range examined; the actual deviation was found to vary with the heat treatment, and cold working.

W. Widder discussed the effect of temp. on the elastic constants, and gave $E=E_{20}\{1-0{\cdot}0006983(\theta-20)\}$. A. Mallock gave 1·12 for the ratio of Young's modulus at −273° to its value at 0°. C. Schaefer observed that for temp. between 20° and −186°, the modulus increased 2463 kgrms. per sq. mm. per 100° difference

of temp. K. R. Koch and C. Dannecker found that the elastic modulus of nickel has a minimum near 100°, a maximum near 300°, another minimum near 1200°, and a maximum near 1250°, indicating a second transformation temp. besides that between 300° and 400°—Fig. 5. J. Zacharias found Young's modulus decreases

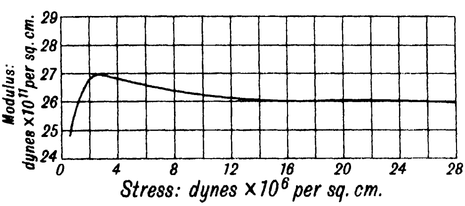


FIG. 4.—Young's Modulus for Small Stresses.

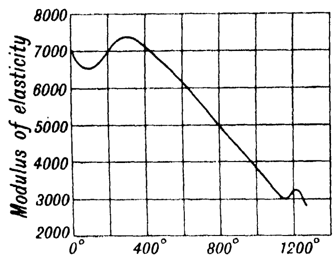


FIG. 5.—The Effect of Temperature on the Elastic Modulus of Nickel.

about 13 per cent. for annealed nickel between 20° and 200°; there is then an increase of about 6 per cent. up to the Curie point; and above the Curie point there is a linear decrease. The results of K. R. Koch and C. Dannecker, and E. P. Harrison, in kgrms. per sq. mm., are, for the torsion and Young's moduli:

	20°	27·5°	96°	110°	200°	300°	400°	600°	1000°	1300°
Torsion .	—	7,300	—	6,430	6,860	1,390	7,120	6,080	3,730	2,480
Young's .	22,000	—	21,300	—	—	—	15,700	—	—	—

E. P. Harrison represented the effect of temp. on the elastic modulus, E, of nickel by $E=E_0(1-0{\cdot}000286\theta-0{\cdot}0_68465\theta^2)$, where $E_0=22{,}200$ kgrms. per sq. mm. up to 300°. Above 325°, the modulus decreases rather more rapidly, reaching a minimum just below 400°; it then remains nearly constant to 425°, above which a rapid decrease occurs. Above 425°, some structural change occurs in which Hooke's law does not apply, for small loads then produce a permanent stretch which does not recover with time. This temp. is near to that at which critical points occur in the magnetism, thermoelectricity, electrical resistance, and thermal expansion. As with steel, the elastic after-effect increases with temp. Loading above a certain value, and subsequently unloading, is followed by a recovery of length, but not of elasticity. K. Honda and T. Terada gave for the elastic modulus of purified nickel $1{\cdot}708\times10^{12}$ dynes per sq. cm. for a load of 1599 grms. per sq. mm., and $1{\cdot}902\times10^{12}$ dynes per sq. cm. for a load of 10,480 grms. per sq. mm.; and for commercial nickel, $1{\cdot}818\times10^{12}$ dynes per sq. cm. for a load of 1376 grms. per sq. mm., and $2{\cdot}212\times10^{12}$ dynes per sq. cm. for a load of 9023 grms. per sq. mm. T. Kawai studied the effect of cold-work on Young's modulus. G. W. Pierce studied the subject. T. Kawai examined the effect of cold-work on Young's modulus—*vide* iron—and found that with the given maximum stress in stretching, kgrms. per sq. mm. (dotted curve, Fig. 6), the corresponding modulus of elasticity, kgrms. per sq. cm. $\times10^{-4}$, were as shown in Fig. 6. The effect of annealing the cold-worked metal at different temp. is also shown in the same diagram, Fig. 6. A. Ancelle studied the subject. M. F. Sayre investigated the elastic after-effect. G. A. Tomlinson discussed the relations between the elastic and cohesive forces; A. L. Bernoulli, J. Kleiber, and A. H. Stuart, the relations between the elastic forces and the sp. ht.; A. Mallock, the relation between the temp. coeff. of the elastic modulus and the m.p.; and

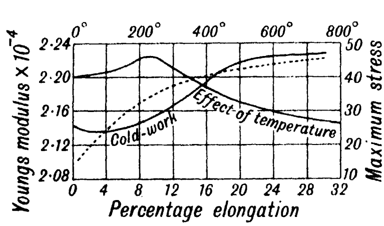


FIG. 6.—The Effect of Cold-work, and of the Temperature of Annealing on the Elastic Modulus of Nickel.

A. Press, E. Grüneisen, S. Ratnowsky, and J. P. Andrews, the relation between the coeff. of thermal expansion, the at. vol., and the elastic constants. B. Bogitch studied the effect of the mode of preparation of nickel on its physical properties. F. C. Thompson and W. E. W. Millington observed that a specimen of nickel for which the elastic limit was 5570 kgrms. per sq. cm. showed slip-bands under a stress of 788 kgrms. per sq. cm.

J. R. Benton gave 0·33 for **Poissan's ratio ;** and A. Wassmuth, K. F. Slotte, and W. Meissner gave 0·30. H. Rolnick calculated Poissan's ratio, ω, from $\omega=0{\cdot}5-\frac{1}{6}Ek$, where E denotes Young's modulus such that $E=20{\cdot}2\times10^{-1}$ c.g.s. units, and k is the compressibility, 0·542 c.g.s. units, consequently $\omega=0{\cdot}318$. E. Grüneisen observed 0·31.

According to W. Gowland, the **tensile strength** of wrought nickel is 42·4 tons per sq. in. W. B. Parker gave 40 to 45 tons per sq. in. for the maximum stress of commercial nickel, and for purified nickel, 18 to 20 tons per sq. in.; the proportional limit for the commercial metal is 18 to 20 tons per sq. in., and for the purified metal, 6 to 10 tons per sq. in.; the elongation in 8 in. is 4·5 to 2 per cent. for the commercial metal, and 8 to 15 per cent. for the purified metal. H. Copaux gave 18,000 lbs. per sq. in. for the tensile strength of nickel—*vide* cobalt; L. Jordan and W. H. Swanger, 46,400 lbs. per sq. in. for 99·94 per cent. nickel; and W. von Selve, 42 kgrms. per sq. mm. and an elongation of 32 per cent. for the metal annealed after rolling. D. H. Browne and J. F. Thompson gave for samples of commercial, malleable nickel: yield-point, when cold-rolled, 90,000 to 110,000, and, when annealed, 20,000 to 30,000 lbs. per sq. in.; tensile strength, when cold-rolled, 100,000 to 120,000, and, when annealed, 60,000 to 90,000 lbs. per sq. in.; elongation in 2 in., when cold-rolled, 15 to 20, and, when annealed, 40 to 50 per cent.; and the reduction of area, when cold-rolled, 40 to 50, and, when annealed, 45 to 55 per cent.

R. A. Hadfield found for the tensile properties expressed in tons per sq. in. to be:

	Elastic limit	Tensile strength	% Elongation in 2 inches	% Reduction of area	Fracture
Cast bar unannealed .	11	16·25	4·50	9·76	Granular
Forged bar unannealed .	14	32·20	45·50	57·04	Fibrous, silky
Forged bar annealed .	7	31·25	54·00	52·50	Fibrous, silky

J. Kollmann gave 38·9 tons per sq. in. for the tenacity of nickel containing 0·05 per cent. of magnesium. Observations were made by H. J. Coe, M. Combe, S. Erk, H. J. French and W. A. Tucker, C. E. Guillaume, T. Kawai, R. Koch and R. Dieterle, P. D. Merica and R. G. Waltenberg, H. F. Moore and T. M. Jasper, W. A. Mudge and L. W. Luff, C. E. Ransley and C. J. Smithells, and A. Schulz.

P. Ludwik, and W. del Regno observed that the tensile strength of nickel gradually falls as the temp. rises until it attains a value of 48·5 kgrms. per sq. mm. at 400°, and it then falls nine times more rapidly to 35·8 kgrms. per sq. mm. at 500°. The break near 400° corresponds with breaks also found in the rigidity, resistance, thermo-electric power, and emissive power. F. Robin found that the maximum brittleness occurred at 300 to 350°; I. M. Bregowsky and L. W. Spring gave for the tensile strength, and yield point in lbs. per sq. in. at different temp.:

	21°	149°	232°	315°	399°	460°	482°	499°	538°
Tensile strength .	38,000	40,900	36,700	35,900	36,600	28,500	27,800	31,900	16,800
Yield point .	23,800	25,100	25,100	22,900	22,600	—	14,200	—	—

and A. le Chatelier gave for the tensile strength, T kgrms., and the elongation, E per cent., of a wire at different temp.:

	15°	100°	150°	200°	250°	300°	350°	400°	460°
T . .	55·2	55·2	55·1	55·0	54·0	51·0	46·0	37·0	30·4
E . .	16	16	16	17	20	21·5	23	21	15

The fall in the tensile strength and the corresponding drop in the elongation and reduction of area have been attributed to an allotropic change corresponding with

the change in magnetic properties. This does not agree with observations on the space-lattice, and Z. Jeffries and R. S. Archer attribute the effect to a spontaneous hardening of the metal, such as occurred with the samples tested by W. P. Sykes for Brinell's hardness. The hardening is attributed to the spontaneous healing of slip-planes formed during deformation. In W. P. Sykes' tests, nickel wires freshly cold-drawn from 0·090 in. to 0·025 in. diameter, were placed in a muffle for heat treatment, or kept in liquid air until tested for the tensile strength, in lbs. per sq. in.—the object of the liquid air treatment was to prevent self-hardening which is known to occur in iron, but very slowly at low temp.:

	Tested after 15 min. in liquid air	250° (45 min. after drawing)			250° (2 hrs. after drawing)		275°		
Time heating . . .		1	5	20	5	15	5	20	30
Tensile strength × 10^{-3}	125·75	126	128	130	128	130·5	130·5	132	131

W. P. Sykes' curves, Fig. 7, discussed by Z. Jeffries and R. S. Archer, for the tensile strength of annealed and cold-drawn nickel show the tendency of the metal to decrease in strength with a rise of temp. The break in the annealed wire between 200° and 300° has just been discussed. The discontinuity with the cold-drawn wire is less apparent. Annealing occurs rapidly between 600° and 800°. The elongation curves for the same wires are shown in Fig. 8. Below the temp. of recrystallization of the annealed wire, there is a general tendency to increasing elongation with decrease of temp. This is interrupted at 200° to 400°, and the minimum in the elongation at 200° corresponds with the horizontal portion of the tensile strength curve. The slight drop in the elongation on cooling from room temp. to the temp. of liquid air is attributed to the beginning of low temp. brittleness. It is probable that at some intermediate temp. the elongation will be higher than at any point on the curve. The elongation of cold-drawn wire increases continuously as it is cooled from 200° down to the temp. of liquid air. There is no drop in elongation at low temp., and this corresponds with the general observation that cold-drawn metals remain ductile at lower temp. than do annealed metals. The rise in elongation in the cold-drawn wire above 400° is due to annealing. The elongation curves, Fig. 9, refer to wire reduced the same amount (61 per cent.) at room temp. and at 400°, respectively. The elongation of the latter is higher in agreement with the general observation that the effect of cold-work is greater the lower is the temp. at which it is effected. There is a distinct minimum in elongation at 300° corresponding with the horizontal zone in the tensile strength curve for annealed nickel. The minimum in the elongation, Fig. 10, is attributed, in part at least, to a blue-heat phenomenon. Observations on the effect of temp.

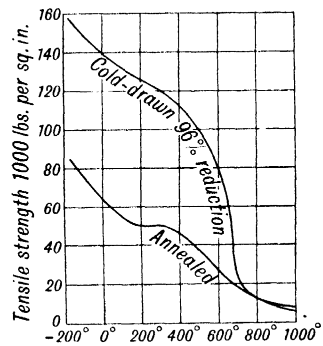
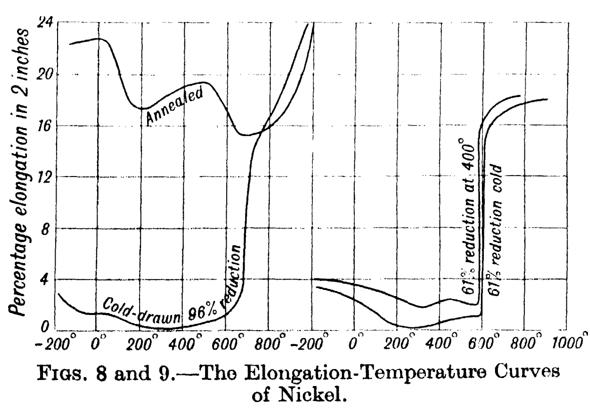


FIG. 7.—The Tensile Strength of Nickel at Different Temperatures.



FIGS. 8 and 9.—The Elongation-Temperature Curves of Nickel.

on the tensile properties of nickel were made by B. Bogitch, A. le Chatelier, P. Chevenard, E. W. Colbeck and W. E. MacGillivray, F. A. Fahrenwald, P. Goerens and P. Mailänder, L. Guillet and J. Cournot, W. J. de Haas and R. Hadfield, D. H. Ingall, K. R. Koch and R. Dieterle, W. Lode, P. Ludwik, W. del Regno, F. Sauerwald and co-workers, W. P. Sykes, H. J. Tapsell and J. Bradley, and C. Upthegrove and A. E. White.

O. Schwarz observed for the effect of rolling, expressed as a percentage reduction, on the tensile strength, expressed in kgrms. per sq. mm.

Reduction .	0	6·0	9·1	20·8	39·5	60·2	80·0	88·0 per cent.
Tenacity . .	43·6	45·1	46·6	54·4	65·2	77·0	84·5	95·1

L. Guillet and co-workers, and M. Weidig observed that annealing the metal at 400° to 800°, and then cooling it in air, reduced its tensile strength, expressed in tons per sq. in.:

	Original metal	Annealed at 400°	600°	800°
Tensile strength	48·0	47·9	40·1	34·5 per cent.
Elongation	3·5	11·0	11·5	32·5 ,,

L. Guillet examined the effect of annealing on the tensile strength of hard-drawn nickel wires. In all cases the temp. of complete annealing corresponded with a rapid fall in the maximum strength and elastic limit, and a rapid increase in the elongation, and it was practically independent of the amount of cold work. The tensile strength, elastic limit, and elongation of hardened nickel are not affected by heating the metal to a temp. below 400°; a slight deflection occurred at about 400°, and a marked alteration between 700° and 750°. The temp. of complete annealing for nickel is between 700° and 750°. L. Guillet also concluded that the effect of time on the annealing process is relatively small. W. B. Price and P. Davidson represented the effect of annealing on the tensile properties of commercial, cold-rolled nickel by the curves, Fig. 10. The tests were made with and across the grain. The annealing range is between 600° to 800°. Commercially, the metal is annealed at about 900°. No difference has been noticed in quick or slow cooling from the annealing temp.

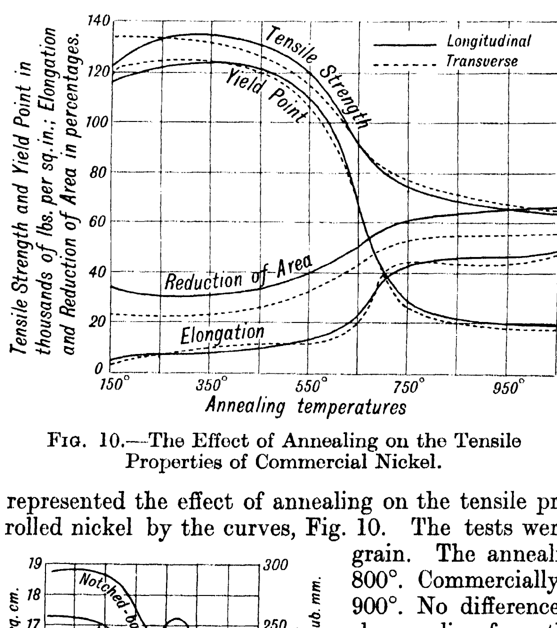


FIG. 10.—The Effect of Annealing on the Tensile Properties of Commercial Nickel.

J. Galibourg, and A. Ancelle studied the effect of ageing on the cold-worked metal at 15°, at 175° to 180°, and at 225° to 235°; J. McNeil, the effect of the casting temp.; F. C. Lea, the effect of hydrogen—*see* iron; P. D. Merica and R. G. Waltenberg, the effect of impurities—*vide infra*, the alloys of nickel; and G. Tammann, the effect of cold-work.

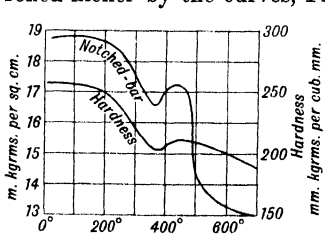


FIG. 11.—Notched-bar Strength and Hardness of Nickel.

F. Sauerwald and T. Sperling studied the notched-bar test, and the results are summarized in Fig. 11. There is a minimum near 380°, and a maximum near 450°, and these singular points also occur in the hardness curve. A. Jacquerod and H. Mügeli observed the bending elasticity of drawn nickel to be 22,100 kgrms. per

sq. mm. at 0°, and of annealed nickel, 20,400 kgrms. per sq. mm. The temp. coeff. between 0° and 100° are, respectively, 0·0003108 and 0·001056. J. Cournot and M. S. Silva found that the creep-stress of nickel is about twice that of steel at temp. between 500° and 700°. P. L. Irwin, H. J. Gough and D. G. Sopwith, G. A. Hankins, H. F. Moore and T. M. Jasper, and J. M. Lessels studied the fatigue and corrosion fatigue strength of nickel. D. J. McAdam obtained data for some static tests, and also for the endurance limit of nickel under cyclic stresses—rotating and alternating torsion. The results are expressed in lbs. per sq. in.:

	Hot-rolled	
	As received	Annealed
Tensile strength	60,500 to 76,200	59,100 to 75,900
Torsional strength	66,300 to 71,100	73,400
Shearing strength	43,500 to 49,700	46,900 to 56,100
Elastic modulus	—	29,400,000
Endurance limit rotating	24,000 to 31,000	—
Endurance limit alternate torsion	—	20,000
	Cold drawn	
	As received	Annealed
Tensile strength	84,500 to 100,800	63,800 to 78,000
Torsional strength	67,000	84,200
Shearing strength	57,500 to 65,600	49,700 to 55,900
Elastic modulus	—	—
Endurance limit rotating	23,000 to 29,000	34,000 to 37,500
Endurance limit alternate torsion	—	19,000
	Cold-rolled	
	As received	Annealed
Tensile strength	115,800 to 166,200	72,400 to 165,500
Torsional strength	81,500 to 96,900	55,700 to 106,900
Shearing strength	65,500 to 94,900	50,400 to 94,900
Elastic modulus	—	—
Endurance limit rotating	25,500 to 40,000	25,500 to 49,000
Endurance limit alternate torsion	17,000	15,000 to 18,000

D. J. McAdam found that samples of cold-rolled, 98·96 per cent. nickel which were given a low temp. anneal to relieve the stress, and also fully annealed, gave the following static mechanical tests:

	Tensile strength	Elastic limit (lbs. per sq. in.)	Proportional limit (lbs. per sq. in.)	Elongation (Per cent. in 2 ins.)	Reduction of area (Per cent.)
Low annealed	131,700	86,000	85,000	16·2	34·1
Fully annealed	77,600	19,300	19,000	49·3	75·2

The simultaneous action of corrosion and fatigue—corrosion-fatigue—may cause failure at stresses far below the ordinary endurance limit—*vide* the corrosion of iron. The results of the tests are represented in the form of graphs of the stress, and the logarithm of the numbers of cycles for failure. The specimens were simultaneously exposed to the action of fatigue and corrosion in air (fatigue curve), fresh, carbonate water, and salt water having about one-third the saline content of sea-water, and stresses alternating at 1450 revs. per minute, gave the results for corrosion-fatigue indicated in Fig. 12. O. Behrens studied the subject.

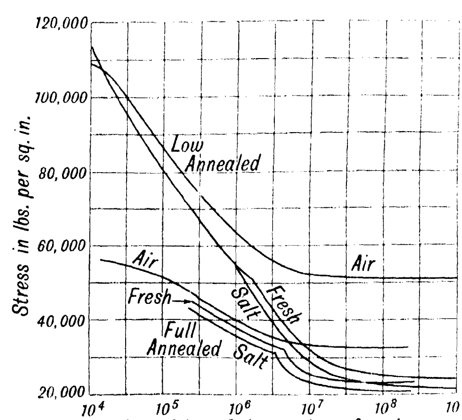


FIG. 12.—The Fatigue and Corrosion-Fatigue of Nickel.

C. Schaefer gave 9518 kgrms. per sq. mm. for the **torsion modulus,** or the

rigidity of nickel; W. Voigt gave 7820 kgrms. per sq. mm.; and E. Grüneisen, A. Wassmuth, K. F. Slotte, and W. Meissner gave 7800 kgrms. per sq. mm. H. Tomlinson obtained 723×10^6 grms. per sq. cm. for the rigidity of hard-drawn and annealed nickel wires. K. Honda and T. Tanaka gave $7{\cdot}50 \times 10^{11}$ dynes per sq. cm. for the rigidity of nickel; and B. Gutenberg and H. Schlechtweg obtained 8×10^{11} dynes per sq. cm. K. Iokibe and S. Sakai found the rigidity of wires of length 27·2 cm., and diameter 0·326 mm., to be

	27°	58°	127°	208°	330°	402°	490°	572°
Rigidity $\times 10^{-11}$.	7·23	7·21	7·09	6·95	6·68	6·31	5·38	4·29

The results are plotted in Fig. 14. The diminution of the rigidity with rise of temp. is relatively small in the ferromagnetic region up to 400°, but above that temp. the decrease is rapid. W. del Regno noted a break in the rigidity-temperature curve near 400°. W. Voigt said that the temp. coeff. of the torsion modulus, in percentages between 20° and —186°, is —3·18. Observations were made by T. Gnesotto and L. A. Alberti, T. Kawai, C. E. Guye and H. Schapper, S. Higuchi, K. Honda and S. Konno, T. Kikuta, G. Subrahmanian, and H. J. Tapsell and J. Bradley. P. W. Bridgman found that with an increase in press. up to 10,000 kgrms. per sq. cm., the rigidity modulus increases 1·84 per cent. W. Lode discussed the rate of flow under the influence of press. and of tension. T. Kawai measured the effect of cold-working on the rigidity of nickel, and obtained the results summarized in Fig. 13 for the metal annealed at 15° and at 100°. K. R. Koch and C. Dannecker's, and E. P. Harrison's results are indicated above, and those of D. J. McAdam, below. T. Lonsdale studied the changes in the dimensions of nickel produced by torsion, and he found that if e denotes the elongation of nickel wire as a percentage of the initial length; T, the twist in turns per cm.; t, the initial torsion in kgrms. per sq. cm.; and D, the diameter in cm., then $e = DT(5{\cdot}8 + 0{\cdot}023t)$. L. di Lazzaro observed that when torsional and tensile stresses are simultaneously applied to nickel, the modulus of torsion is diminished, and restored when the tension is released. C. Schaefer observed that the relation between the torsion modulus and the m.p. is the same as that observed between the hardness and the m.p.; and D. Schenk studied the effect of torsional oscillations on the rigidity of nickel.

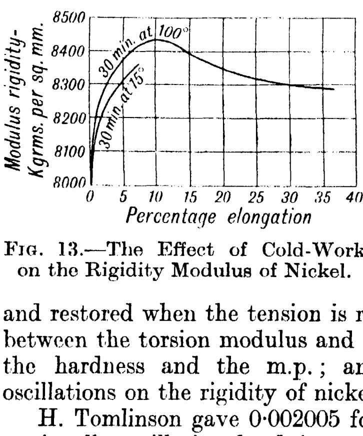


FIG. 13.—The Effect of Cold-Work on the Rigidity Modulus of Nickel.

H. Tomlinson gave 0·002005 for the **logarithmic decrement** (base 10), λ, of a torsionally-oscillating, hard-drawn nickel wire, and for the annealed wire, 0·000852. K. Iokibe and S. Sakai measured the logarithmic decrement of nickel wires at different temp., and for wires with the moment of inertia 33,358 grms. per sq. cm., length 27·2 cm., and diameter 0·326 mm., they found

	22°	72°	115°	205°	239°	338°	492°	546°
$\lambda \times 10^5$ . . .	160	147	151	180	163	252	2730	4130

The results are plotted in Fig. 14. For ordinary temp., and up to 80°, the logarithmic decrement decreases; then increases to a maximum at 160°; decreases slightly to 250°, and then increases rapidly. The existence of the maximum is a resultant of the increasing effect due to temp., and the decreasing effect due to the magnetic transformation of nickel. J. Cournot and M. S. Silva, and M. Ishimoto also studied the internal viscosity of nickel; and T. Gnesotto and L. A. Alberti, and K. Honda and S. Konno, the rigidity and viscosity at the Curie point.

T. W. Richards gave $\beta = 0{\cdot}0_6 43$ for the average **compressibility** of nickel at 20° between 100 and 500 megabars press.; L. H. Adams gave $\beta = 0{\cdot}0_6 54$, and for $d\beta/dp$, $-0{\cdot}0_{11}4$; R. F. Mehl gave $\beta = 0{\cdot}0_6 495$; and P. W. Bridgman gave $\beta = 0{\cdot}0_6 516$ up to 12,000 kgrms. press. per sq. cm. The low result obtained by T. W. Richards

is attributed to the internal strains introduced by the heavy forging which was found necessary to eliminate flaws in the metal. P. W. Bridgman observed for commercial nickel rods, at 30°, $\delta v/v_0=-0{\cdot}0_6525p+0{\cdot}0_{11}21p^2$ and, at 75°, $\delta v/v_0=-0{\cdot}0_6528p+0{\cdot}0_{11}21p^2$; and for drawn wire of the purified metal, at 30°, $\delta v/v_0=-0{\cdot}0_6529p+0{\cdot}0_{11}21p^2$; and, at 75°, $\delta v/v_0=-0{\cdot}0_6535p+0{\cdot}0_{11}21p^2$. T. W. Richards gave 508 kilomegabars. J. P. Andrews, E. Grüneisen, S. Ratnowsky, and A. Press discussed the relation between the coeff. of thermal expansion, the at. vol., and the isothermal compressibility; and F. Bergfeld, the relations between compression and tension when the nickel is considered as a liquid of great tenacity.

R. F. Mehl gave 508 kilomegabars for the **internal pressure** of nickel, and 1890 kgrms. per sq. mm. for the maximum disruptive internal pressure. I. Traube, and J. H. Hildebrand and co-workers calculated relative values for the internal press. of the elements. R. von Dallwitz-Wegner gave 315,558 to 357,140 atm. for the **cohesive pressure** of nickel at 0°, and 212,020 to 301,948 atm. at 100°. M. Born and O. F. Bollnow calculated the cohesive force between the atoms in the space-lattice to be $3{\cdot}6\times10^{11}$ dynes per sq. cm.

W. Lode, W. Rohn, G. Sachs, and F. C. Thompson and W. E. W. Millington discussed the **plastic flow** of nickel; and J. Garnier, the **fluidity.** A. L. Kimball and D. E. Lovell gave $1{\cdot}55\times10^{15}$ c.g.s. units for the **internal friction** of the cold-rolled metal; and B. Gutenberg and H. Schlechtweg gave 2×10^8 c.g.s. units for the internal friction. K. Honda and S. Konno gave $0{\cdot}722\times10^8$ for the coeff. of **viscosity** of rolled nickel. J. Garnier, T. Gnesotto and L. A. Alberti, and W. Sutherland made observations on the viscosity of the metal; and J. Cournot and S. Silva found that the viscosity of nickel at 500° to 600° is nearly double that of an ordinary soft, or semi-soft steel. K. Iokibe and S. Sakai studied the effect of temperature. S. Sato measured the internal energy due to cold-work. P. E. Shaw and E. W. L. Leavey studied the **friction** of nickel in vacuo against nickel, copper, silver, aluminium, and iron; and observations were also made by G. A. Tomlinson.

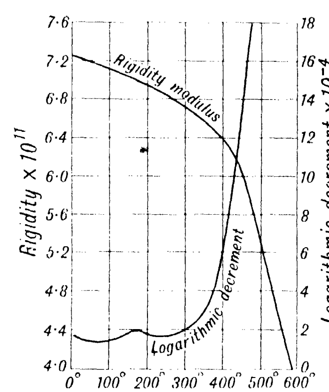


FIG. 14.—The Rigidity and Logarithmic Decrement of Nickel at different Temperature.

The change in size of cast-nickel between the customary pouring temp. and room temp. was found by D. H. Browne and J. F. Thompson [4] to be about ¼ in. per foot—or 0·244 in. per foot. N. B. Pilling and T. Kihlgren also studied the casting shrinkage of nickel and its alloys. The coeff. of **thermal expansion** of nickel is very near to that of steel. This is of great practical importance, because it allows the two metals to be used in conjunction under conditions of varying temp. without distortion or relative changes of size or shape. W. H. Souder and P. Hidnert found that the average coeff. of expansion of ten samples of commercial nickel varied from $0{\cdot}0_4129$ to $0{\cdot}0_4135$ for the range 25° to 100°, and these data are approximately 10 to 20 per cent. greater than those for ordinary steel in the same range of temp. E. Grüneisen gave for a rod a metre long at 0°, up to 1000°, $\delta l=1000\{0{\cdot}0_413460(\theta_2-\theta_1)+0{\cdot}0_83315(\theta_2 2-\theta_1 2)\}$ mm.; and for the coeff. of expansion, he gave $\alpha=0{\cdot}0_41021$ between $-190°$ and 17°, and $0{\cdot}0_41335$ between 17° and 100°. H. Donaldson gave for the length of a rod at $\theta°$ which is unit length at 0°, $l\times10^{-6}=1+0{\cdot}35\theta+0{\cdot}0016\theta^2$. H. Fizeau observed that the coeff. of linear, thermal expansion for nickel reduced by hydrogen and compressed is 0·00001279 at 40°. This value increases $0{\cdot}0_871$ for each degree variation of temp. R. von Dallwitz-Wegner gave $0{\cdot}0_4357$ to $0{\cdot}0_4444$ for the cubic coeff. at 0°, and $0{\cdot}0_4419$ to $0{\cdot}0_4468$ at 100°.

H. le Chatelier gave $0{\cdot}0_4125$ for the coeff. of expansion of nickel at ordinary temp., and $0{\cdot}0_4130$ at 1000° ; W. Voigt, for the expansion of unit length at $\theta°$, $0{\cdot}0_41315+0{\cdot}0_7413(\theta-30)$; J. A. N. Friend and R. H. Vallance, $0{\cdot}0_4133$, between 10° and 100° ; H. Masumoto, $0{\cdot}0_41276$ for electrolytic nickel, and $0{\cdot}0_41290$ for Mond nickel ; H. Masumoto and S. Nara, $0{\cdot}0_41358$, between 30° and 100° ; A. E. H. Tutton, for nickel reduced from carbonyl, $0{\cdot}0_41248+0{\cdot}0_7148\theta$. L. Holborn and A. L. Day found for the average coeff. of expansion between 0° and 250° was $0{\cdot}0_4138$; three days later, $0{\cdot}0_4139$; and five days later, $0{\cdot}0_4142$; between 250° and 375°, the coeff. was $0{\cdot}0_4162$; between 250° and 500°, $0{\cdot}0_4162$, and five days later, $0{\cdot}0_4162$; between 375° and 500°, $0{\cdot}0_4164$; between 500° and 750°, $0{\cdot}0_4179$, and five days later, $0{\cdot}0_4179$; between 0° and 750°, $0{\cdot}0_4159$, and the same five days later ; and between 750° and 1000°, $0{\cdot}0_4192$, and the same five days later. They represented the results by $0{\cdot}0_413460\theta+0{\cdot}0_833156\theta^2$ for temp. above 375°. F. Henning gave $0{\cdot}0_41031$ between −191° and 16° ; and

	−198° to 16°	16° to 250°	16° to 375°	16° to 500°	500° to 750°	500 to 1000°
a . .	$0{\cdot}0_4101$	$0{\cdot}0_4140$	$0{\cdot}0_4147$	$0{\cdot}0_4152$	$0{\cdot}0_4176$	$0{\cdot}0_4184$

Observations were made by N. L. Mochel, A. Eucken and W. Dannöhi, C. Williams, and P. Chevenard. P. Hidnert gave for the average coeff. of thermal expansion, a, for 99·94 per cent. nickel :

	25° to 100°	25° to 300°	300° to 600°	600° to 900°
$a\times10^{-6}$	13·3	14·4	16·5	17·8

There is an irregularity in the region near 350°. C. E. Guillaume obtained for purified nickel of commerce, $0{\cdot}0_412666+0{\cdot}0_85420\theta$; and for various samples of commercial nickel, the coeff. ranged from $0{\cdot}0_412491+0{\cdot}0_87020\theta$ to $0{\cdot}0_4655+0{\cdot}0_85500\theta$. A. Krupkowsky gave for the mean coeff. of linear expansion of nickel, $8{\cdot}10\times10^{-6}$ between −252·6 and 10° ; $10{\cdot}12\times10^{-6}$ between −183° and 10° ; $14{\cdot}04\times10^{-6}$ between 18° and 217° ; and $15{\cdot}11\times10^{-6}$ between 18° and 444° ; whilst for the coeff. a and $2b$ in $l=l_0(1+a\theta+b\theta^2)$ he obtained between −183° and 217°, $a=11{\cdot}86\times10^{-8}$ and $2b=2{\cdot}01\times10^{-6}$; and between 18° and 444°, $a=12{\cdot}83\times10^{-6}$ and $2b=1{\cdot}03\times10^{-8}$. C. E. Guillaume observed that the thermal expansion of commercial nickel of 1911 was distinctly lower than that of some 1891 samples. J. Disch found for the linear expansion in mm. per metre between 0° and $\theta°$:

	−190°	−78°	0°	100°	200°	300°
Expansion .	−1·885	−0·92	0	1·30	2·735	4·30 mm. per m.

W. H. Souder and P. Hidnert found that the annealing of hot-rolled samples (Ni, 99·02 ; C, 0·08 ; Cu, 0·12 ; Fe, 0·37 ; Mn, 0·22 ; Si, 0·16) generally caused a slight increase in the coeff. of thermal expansion. The average coeff. between 25° and 300° for samples containing 98·76 to 99·06 per cent. nickel are $0{\cdot}0_4144$ for the hot-rolled and $0{\cdot}0_4145$ for the annealed samples. For the range 25° to 600°, the coeff. of five hot-rolled samples varied from $0{\cdot}0_4149$ to $0{\cdot}0_4156$, and for five annealed specimens from $0{\cdot}0_4154$ to $0{\cdot}0_4157$. They represented their observations on the expansion and contraction of rods of commercial nickel by the curve, Fig. 15. Only a slight irregularity was perceptible in the region of 350°, but no marked change occurs. This agrees with E. P. Harrison's statement that the effect with impure metals may be masked or modified by changes of a chemical nature. H. Wedding observed no essential difference in the thermal expansion of cast and wrought nickel.

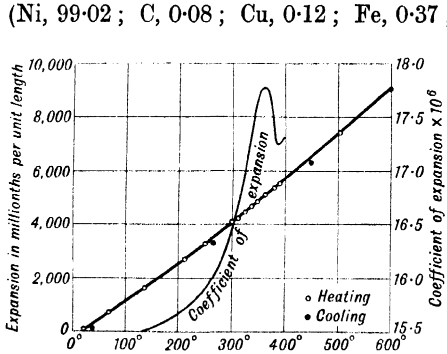


FIG. 15.—Thermal Expansion of Commercial Nickel.

F. Simon and R. Bergmann's results for the coeff. of thermal expansion of nickel between $-178°$ and $2°$ are indicated in Fig. 16. F. L. Uffelmann's values of the coeff. of thermal expansion on heating and cooling curves are indicated in Fig. 17. G. A. Tomlinson discussed the relations between the interatomic forces and the thermal expansion. E. P. Harrison found for purified nickel for temp. up to 300°, $0{\cdot}0_4 1280+0{\cdot}0_5 75\theta+0{\cdot}0_{10}35\theta^2$, and for the coeff. between 0° and 50°, $0{\cdot}0_4 128$; 50° and 100°, $0{\cdot}0_4 136$; 150° and 200°, $0{\cdot}0_4 151$; 250° and 300°, $0{\cdot}0_4 174$; 300° and 350°, $0{\cdot}0_4 191$; and 350° and 365°, $0{\cdot}0_4 205$; 380° and 400°, $0{\cdot}0_4 191$; 400° and 450°, $0{\cdot}0_4 189$; 450° and 500°, $0{\cdot}0_4 192$; and 500° and 550°, $0{\cdot}0_4 190$.

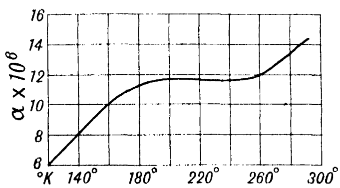


FIG. 16.—Coefficient of Thermal Expansion of Nickel.

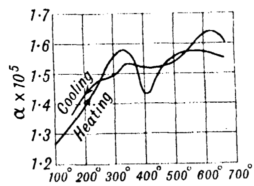


FIG. 17.—Coefficient of Thermal Expansion on Rising and Falling Temperatures.

E. P. Harrison added that up to about 365°, the curve is regular, but between 365° and 380° there is an anomalous change in the expansion, whilst above 380° the curve is again regular and linear, with a different shape from the part which precedes it. No difference in the position or shape of the anomalous portion of this curve was noticed, whether the temp. was rising or falling, and in every case the wire returned after heating to its original length. There was no permanent elongation. The anomalous portion of the curve extends from 340° to 370°, and it is approximately the range over which changes occur in the thermoelectric force, electrical resistance, and magnetic permeability—the magnetic susceptibility vanishes at 370°. The anomalous change in the expansion was attributed to changes in the metal itself; though with impure metals, the true effect might be masked or modified by changes of a chemical nature. E. Jänecke observed a break in the expansion curve at 347° to 360°, but M. Werner observed no abrupt change in volume. H. M. Randall's, and H. F. Colby's measurements indicated a critical region in the thermal expansion of nickel between 280° and 370°. W. F. Barrett observed an anomalous momentary expansion occurred in the cooling of a nickel wire, and this was coincident with a temporary, spontaneous re-heating of the wire. L. Holborn and A. L. Day said that a transformation occurs at about 370°, and that a rod originally 482·6 mm. at 0° was approximately 0·02 mm. shorter after each test. Observations were made by W. P. Davey. W. F. Colby measured the coeff. of thermal expansion of nickel in the neighbourhood of the Curie point, 374°, and the results are summarized in Fig. 15. Whilst iron shows an anomalous increase in passing from the non-magnetic to the magnetic state, nickel shows an anomalous contraction. F. C. Powell calculated the contraction at 220° to be $dl/l=-0{\cdot}9\times10^{-4}$—*vide* iron.

W. H. Souder and P. Hidnert also observed that after heating to 600° and cooling rods of commercial nickel to atm. temp., the rods were 0·004 to 0·065 per cent. shorter than before. E. P. Harrison observed no change with purified nickel; and H. G. Jones found that when nickel is quenched from 525°, it contracts for about 10 min., and for some hours it suffers very little change in length, but, after that, a gradual contraction occurs. A. Merz discussed the subject. A. Press, J. P. Andrews, E. Grüneisen, and S. Ratnowsky studied the relation between the thermal expansion, compressibility, and at. vol.

W. F. Barrett [5] found the **thermal conductivity** of nickel to be 0·131 when that of silver is unity. L. R. Ingersoll gave 0·1428 c.g.s. units for the thermal conductivity of nickel; W. Jäger and H. Diesselhorst found for Ni, 97; Co, 1·4; Mn,

1·0; Fe, 0·4; C, 0·1; and Si, 0·1, the conductivity 0·140 at 18°, 0·129 at −160°, and 0·1384 at 100°, and the temp. coeff. −0·31 per cent.; E. H. Hall gave for Ni, 85·4; Fe, 7·6; and Si, 0·4, 0·106 at 116°; and W. C. Ellis and co-workers, 0·168 cal. per cm. per sec. per degree; C. H. Lees obtained for 99 per cent. nickel, 0·129 at −160°, and 0·140 at 18°; K. Honda, 0·0833 at 30°; and H. Masumoto, 0·1821 at 30°. T. C. Baillie observed for the conductivity, k in c.g.s. units, of Ni, 97·22; Fe, 0·75; Mn, 1·68; and Mg, 0·28:

	40°	60°	80°	100°	120°	140°	150°
k . . .	0·118	0·125	0·133	0·137	0·139	0·140	0·142

Measurements were made by M. S. van Dusen and S. M. Shelton. F. H. Schofield's values in c.g.s. units, at different temp., were:

	100°	140°	196°	290°	355°	491°	703°	733°
k . .	0·145	0·144	0·138	0·128	0·128	0·128	0·136	0·133

R. H. Frazier studied $k/c=1·3269\pm0·0012$, where c denotes the sp. ht. M. F. Angell gave 0·126 at 300°; 0·104 at 500°; 0·069 at 700°; 0·065 at 950°; and 0·058 at 1200°. His results, plotted in Fig. 18, show a break in the curve near 700°. This break was not observed by K. Honda and T. Simidu, who found, for k in c.g.s. units:

	0°	100°	200°	300°	400°	500°	600°	700°	800°	900°
k .	(0·132)	0·132	0·130	0·124	0·117	0·123	0·130	0·135	0·140	(0·142)

P. W. Bridgman measured the effect of pressure on the thermal conductivity and found a linear decrease of 14·1 per cent. for a press. of 12,000 kgrms. per sq. cm. The press. coeff. of the thermal conductivity is $-0·0_412$; and in tension, under a load of 1900 kgrms. per sq. cm., the proportional change of the thermal conductivity is 0·076 per cent., or $0·0_640$ kgrm. per sq. cm. F. Gäbler, R. Kikuchi, and M. Jakob studied the subject; and K. Dittrich, M. Jakob and S. Erk, and G. F. Sager, the application of Wiedemann and Franz's conductivity law—*vide infra*, nickel-copper alloys. A. Johnstone found that the thermal conductivity is raised above 0·5 per cent. by a tension of about 0·7 of the elastic limit, and the original conductivity is restored when the tension is withdrawn. G. Tammann and W. Boehme found that the thermal conductivity is decreased by cold-working the metal.

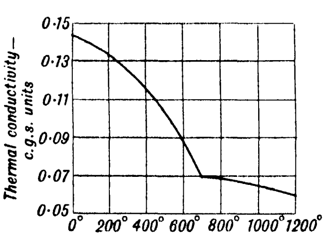


FIG. 18.—The Thermal Conductivity of Nickel.

J. Dalton [6] gave 0·10 for the **specific heat** of nickel, and P. L. Dulong and A. T. Petit gave 0·1035. H. V. Regnault found the sp. ht. of nickel containing some carbon to be 0·11095 between 21° and 98°; and for a sample of a higher degree of purity, 0·1108 between 12° and 97°. Another sample gave 0·10752 between 17° and 97°. W. F. Barrett gave 0·1091 for the sp. ht. of nickel; and L. R. Ingersoll, 0·1168 between 25° and 100°; W. Voigt, 0·1084 for the sp. ht. of a sample of commercial nickel; P. Schübel, 0·1086 between 18° and 100°, and 0·1254 between 18° and 600°; H. Copaux, 0·108 between 20° and 100°; W. Jäger and H. Diesselhorst, 0·1065 at 18°, and 0·1159 at 100°; H. E. Schmitz, for nickel with Co, 0·9; Fe, 0·6; and Cu, 0·7, between the b.p. of liquid oxygen and 0°, 0·0826, and between 20° and 100°, 0·1094; and A. Naccari:

	18°	50°	100°	150°	200°	250°	300°
Sp. ht. . . .	0·1057	0·1090	0·1137	0·1185	0·1232	0·1279	0·1327

or $c=0·10596+0·0_4946(\theta-15)$. W. A. Tilden obtained for nickel prepared from nickel carbonyl, and fused in hydrogen, between 15° and

	−182°	−78°	100°	185°	350°	415°	435°	550°	630°
c .	0·0838	0·0975	0·1084	0·1101	0·1186	0·1227	0·1240	0·1240	0·1246

W. H. Keesom and C. W. Clark studied the atomic heat between $-271 \cdot 9°$ and $-254°$. W. Schlett found between 0° and

	20·86°	50·41°	101·37°	110·50°	200°	309°
c . . .	0·10347	0·10534	0·10790	0·10842	0·11190	0·11740

or $c=0 \cdot 10280+0 \cdot 000047010$. F. Wüst and co-workers found that from 0° to 320° the mean sp. ht. is $0 \cdot 10950+0 \cdot 0_4 5240\theta$, and the true sp. ht., $0 \cdot 10950+0 \cdot 0_3 148\theta$; between 330° and 1451° the mean sp. ht. is $0 \cdot 41\theta^{-1}+0 \cdot 12931+0 \cdot 0_6 11\theta$, and the true sp. ht., $0 \cdot 12931+0 \cdot 0_6 22\theta$. P. N. Beck obtained:

	124°	198°	248°	295°	318°	340°	350°	361°
c .	0·11278	0·11530	0·11879	0·12151	0·12288	0·12379	0·12500	0·12583

or $c=0 \cdot 095451+0 \cdot 0_3 23\theta-0 \cdot 0_6 3072\theta^2$ between 0° and 361°; and between 376° and 800° $c=0 \cdot 155485-0 \cdot 0_3 12892\theta+0 \cdot 0_6 15859\theta^2$, or

	376°	400°	445°	500°	599°	648°	752°	800°
c .	0·12692	0·12686	0·12703	0·12732	0·21821	0·12877	0·13107	0·13195

A. Dumas gave for the sp. ht. of purified nickel between 17° and

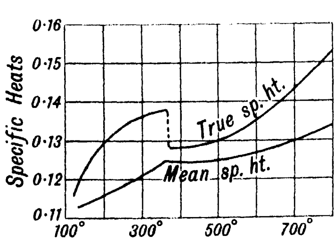
	98°	197°	266°	321°	366°	406°	595°	612°
c . .	0·1090	0·1118	0·1145	0·1174	0·1200	0·1208	0·1221	0·1221

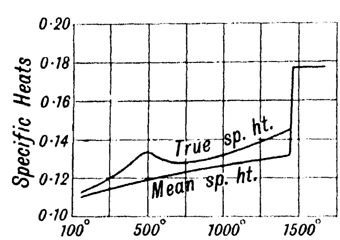
G. Tammann and A. Rohmann gave for the heat capacity, c_{100} cals. per gram-atom:

	−200° to −100°	−100° to 0°	0° to 100°	100° to 200°	200° to 300°	300° to 400°	400° to 500
c_{100} .	384·36	548·07	635·89	665·43	695·36	737·02	741·72

H. Schimpff gave 0·1092 for the sp. ht. between 17° and 100°, 0·0975 between 17° and −79°, and 0·0829 between 17° and −190°; U. Behn, for 98 per cent. nickel, 0·0572 at −186°, 0·0888 at −79°, 0·0934 at 0°, and 0·1053 at 18°; T. W. Richards and F. G. Jackson, 0·0869 between 19·6° and −185·6°; P. Nordmeyer and A. L. Bernoulli, 0·0918 between 20° and −185°; J. Dewar, 0·0208 between −253° and −196°; and E. Grüneisen gave c_p=0·0844 between −190° and 17°; and 0·1094 between 17° and 100°. F. Simon and M. Ruhemann, E. Ahrens, N. F. Mott, and M. S. van Dusen and S. M. Shelton studied the subject.

W. Geiss and J. A. M. van Liempt showed that the temp. coeff. of the sp. ht. of cold-drawn nickel is 0·00505, and of nickel annealed at 1000°, 0·00636; and the sp. hts. are, respectively, 0·1035 and 0·1036, so that the difference is outside the range of measurement. M. A. Audins found that the sp. ht. of nickel is slightly increased by permanent deformation; and W. Schlett, that the sp. ht. of nickel cold-drawn from 2 mm. to 0·36 mm. is 0·1068 (sp. gr. 8·8209) when that of the annealed metal is 0·1057 (sp. gr. 8·8442). The more dense the metal, the lower sp. ht. The results are plotted in Fig. 19. It is inferred that a rise of temp. causes





FIGS. 19 and 20.—The Specific Heat of Nickel.

molecular changes to take place which are very different from those brought about by mechanical treatment.

J. Pionchon obtained 0·10836 at 0°, 0·117292 at 200°, 0·1300 at 250°, 0·126 at 400°, 0·15759 at 350°, and 0·1665 at 1000°. He said that there are breaks in the curve at 230° and at 400°, so that he represented the sp. ht. between 0° and 230° by

$c=0{\cdot}10836+0{\cdot}0_4 4466\theta$, between 230° and 400° by $c=0{\cdot}183493+0{\cdot}0_3 564\theta+0{\cdot}0_5 1399998\theta^2$, and between 400° and 1150° by $c=0{\cdot}099+0{\cdot}0_4 6175\theta$. P. Weiss and co-workers found the maximum sp. ht. to be 0·1527 between 361° and 376°. They gave for the variation in the thermal capacity, Q, with temp., θ, that is, the sp. ht.:

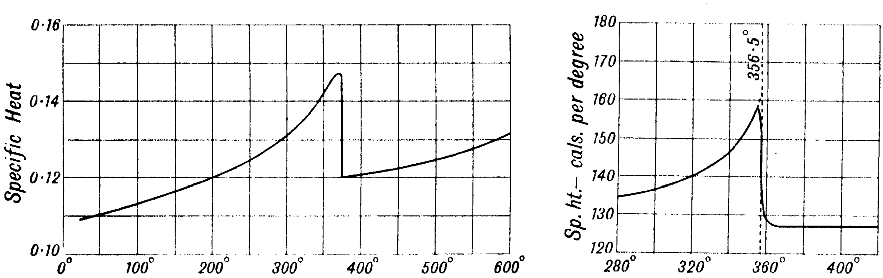
	17°	123·7°	247·7°	350°	375·6°	400°	500·2	705·2°	751·6°	799·6°
$dQ/d\theta$.	0·0977	0·1124	0·1316	0·1457	0·1527	0·1259	0·1330	0·1391	0·1526	0·1445

The part of the sp. ht. due to demagnetization is estimated to be 0·025. The subject was discussed by P. Weiss, L. F. Bates, K. E. Grew, W. M. Latimer, M. Gaudino, F. Simon, and C. Schwarz. Measurements were also made by E. Horn, and C. Drucker. For A. W. Foster's observations, *see* the nickel-chromium alloys. H. Klinhardt found a maximum in the sp. ht. at 360° corresponding with the Curie point—*vide* iron—but, added W. Sucksmith and H. H. Potter, contrary to P. Weiss' theory of ferromagnetism, beyond that point the sp. ht. falls continuously and not discontinuously. S. Umino's values for the mean and true sp. ht. plotted roughly in Fig. 20, are

	100°	200°	300°	390°	500°	600°	700°	800°	900°
Mean .	0·1079	0·1107	0·1134	0·1173	0·1203	0·1216	0·1218	0·1220	0·1228
True .	0·111	0·116	0·122	0·131	0·134	0·123	0·124	0·126	0·130

	1000°	1100°	1200°	1250°	1300°	1400°	1500°	1550°	1650°
Mean .	0·1243	0·1251	0·1265	0·1270	0·1279	0·1289	0·1783	0·1783	0·1783
True .	0·132	0·134	0·136	—	0·139	0·142	0·181	0·181	0·181

There is thus, as with other ferromagnetic metals, an abnormal change in the ferromagnetic range, $C_p=6{\cdot}25+0{\cdot}001147T$. The results of A. Dumas, and of J. Dorfman and R. Jaanus are summarized in Figs. 21 and 22. C. Lapp observed



FIGS. 21 and 22.—The Specific Heats of Nickel at Different Temperatures.

between —175° and 460°, a rise towards the Curie point with a region between 353·5° and 360°, where the curve is discontinuous, and a paramagnetic region where the sp. ht. rises slowly—*cf.* Fig. 22, magnetism.

A. Eucken and co-workers obtained for the **atomic heat** of recrystallized nickel at constant press. and temp., and for Debye's constant Θ—the x of **1.** 13, 14—the values:

T° K.	15·05°	18·06°	40·93°	82·30°	123·96°	168·74°	185·57°	204·05°
C_p .	0·04646	0·06260	0·5637	2·536	4·000	4·975	5·205	5·432
C_v .	0·04646	0·06260	0·5635	2·530	3·976	4·924	5·144	5·359
Θ .	324	353	378	357	368	334	323	300

and for pressed nickel:

T° K.	17·70°	22·30°	32·25°	84·90°	139·32°	171·76°	175·23°	188·51°
C_p .	0·05577	0·0917	0·2819	2·638	4·402	5·005	5·053	5·232
C_v .	0·0558	0·0917	0·282	2·631	4·369	4·953	4·999	5·169
Θ .	361	383	379	376	359	337	335	332

F. M. Jäger gave 6·34 Cals. for the at. ht., C_p, of nickel at 50°; at 100°, 6·65 Cals. for C_p and 6·30 for C_v; at 365°, 7·95 Cals. for C_p and 7·13 Cals. for C_v. For β-nickel C_p is 7·30 to 7·40 Cals. up to 600°, and C_v, 6·38 to 6·18 Cals. H. A. Jones

and co-workers gave for the at. ht. of nickel at a temp. T° K., $C_p=4{\cdot}39+0{\cdot}00411T$. The values calculated from the sp. hts. of J. Dewar, W. Jäger and H. Diesselhorst, U. Behn, and J. Piochon are :

	−253°	−186°	−79°	18°	100°	800°	1000°
Atomic heat . .	1·22	4·30	5·80	6·24	6·80	7·36	8·71

I. Maydel gave for the at. ht. $C_p=8{\cdot}639-938{\cdot}9(\theta+354)^{-1}$. W. H. Rodebush and J. C. Michalek found the values for the at. ht., C_p, of nickel at low temp. agree very closely with those for iron :

	−203°	−190°	−183°	−173°	−73°	25°
C_p	1·980	2·480	2·900	3·300	5·52	7·24

E. D. Eastman and co-workers calculated $C_p-C_v=0{\cdot}16$ Cal. per degree per mol. F. Wüst and co-workers gave $50{\cdot}21\theta^{-1}+0{\cdot}13380$ for the mean sp. ht. of the molten metal between 1451° and 1520°, and for the true sp. ht. 0·13380. S. Umino observed no variation of the true sp. ht. of nickel with temp. after fusion. G. A. Tomlinson discussed the relations between the sp. ht. and the interatomic forces; A. L. Bernoulli, and A. H. Stuart, the relations between the elastic constants and the sp. ht. ; and P. S. Epstein, and J. R. Ashworth, the relations between the thermal and magnetic constants.

J. B. Richter,[7] and R. Tupputi said that nickel is as easily melted as is manganese ; O. L. Erdmann, that it is as easily melted as cast-iron ; and L. Thompson, that it is more easily melted than cobalt and iron. The oxidation of the metal while molten was discussed by C. L. Winkler, I. Wharton, and C. W. Siemens and A. K. Huntington ; R. Ruer and K. Kaneko found that molten nickel dissolves the oxide, the f.p. is accordingly lowered, and the metal rendered brittle. L. Pebal discussed the ready union of the molten metal with carbon. R. C. Smith found that filings of the metal sintered at 650°, and the precipitated metal at 700°. A. Schertel gave 1392° to 1420° for the **melting point** of nickel ; R. Pictet gave 1450°. P. H. van der Weyde, and T. Carnelley somehow got wide of the mark, for they gave 1600° for the m.p. of the metal. H. le Chatelier gave 1420° ; H. Copaux, 1470° ; E. M. Terry, and O. Ruff and W. Bormann, 1452° ; G. K. Burgess and R. G. Waltenberg, 1452° ; A. L. Day and R. B. Sosman, 1452·3° ; L. Holborn and W. Wein, 1484° ; G. Petrenko, and M. Levin, 1484° ; A. G. C. Gwyer, W. Guertler and G. Tammann, N. Konstantinoff, K. Losseff, H. Giebelhausen, A. D. Dourdine, and G. Voss, 1451° ; K. Friedrich, 1484° ; N. Baar, 1456° ; S. F. Schemtschuschny and co-workers, 1484° ; G. K. Burgess, 1435° for 99·95 per cent. nickel ; C. G. Fink and F. A. Rohrman, 1458° ; H. C. Cross, 1455° ; and L. Jordan and W. H. Swanger, and H. T. Wensel and W. F. Roeser, 1455°± for the m.p. or f.p. of 99·94 per cent. nickel. W. Guertler and M. Pirani, and L. I. Dana and P. D. Foote gave 1452° for the best representative value. T. Carnelley discussed the relation between the m.p. and the coeff. of thermal expansion ; and K. Honda and H. Masumoto, and G. A. Tomlinson, the relation between the m.p. and the interatomic forces ; W. Crossley, the relation between the at. vol. and the m.p. ; A. Stein, the relation between the resistance and the m.p. ; R. Forrer, the relation between the m.p. and the lattice structure ; and J. A. M. van Liempt and J. A. de Vriend, the time of melting thin fuses.

W. Crookes estimated the volatility of nickel to be 10·99 when that of gold is 100 ; W. N. Hartley observed that nickel is volatile in the oxy-hydrogen flame ; and H. Moissan showed that nickel distils in the electric furnace more readily than cobalt. 150 grms. were distilled in 5 min., in an electric arc furnace, and 200 grms. in 9 min. O. Ruff and W. Bormann gave 2340° for the **boiling point** of nickel under 30 mm. press. W. R. Mott estimated the b.p. to be 2700° ; H. A. Jones and co-workers, 3377° ; and R. W. Millar calculated 3075° at 760 mm., 2950° at 500 mm., 2560° at 100 mm., and 1840° at 1 mm. press. H. A. Jones and co-workers calculated the b.p. to be 3377°. O. Ruff and co-workers said that an alloy saturated with carbon begins to boil at about 12,500°. R. W. Millar represented the **vapour pressure,** p mm., of molten nickel by $\log p=-1{\cdot}448 \log T$

$-18340T^{-1}+13\cdot451$. H. A. Jones and co-workers calculated values for the rate of evaporation, m, of nickel filaments, $\log_{10} m=40\cdot218/4\cdot577-(85100+400)/4\cdot577T-(0\cdot971/4\cdot577)\log_{10}T-0\cdot00206T/4\cdot577-4340/4\cdot577\times1725$; and for the vap. press., p, $\log_{10} p = 40\cdot218/4\cdot577+3\cdot475-(4340+400)/4\cdot577\times1725-(0\cdot971-0\cdot5)\log_{10}T-0\cdot00206T/4\cdot577$; or

T° K.	500°	1000°	1500°	2000°	2600°	3000°	3650°
p .	$1\cdot62\times10^{-20}$	$1\cdot34\times10^{-7}$	$2\cdot94\times10^{-1}$	$2\cdot9\times10^{2}$	$2\cdot4\times10^{4}$	$1\cdot6\times10^{5}$	$1\cdot0\times10^{6}$

Nickel becomes non-magnetic when heated above about 350°. J. Plücker [8] observed that the magnetic power of nickel is five times smaller at 350° than it is at 50°. E. Becquerel added that the magnetic power of nickel is completely lost at 400°. Whilst iron undergoes transformations at about 890° and 770°—*vide* iron—cobalt undergoes a magnetic transformation at about 1143°, and nickel at about 340°, when magnetic, or α-nickel passes into the non-magnetic, or β-nickel. The corresponding transformation with iron is lowered continuously by increasing proportions of nickel up to 25 per cent., so that C. E. Guillaume suggested that α-iron and α-nickel are isomorphous. Similarly, the behaviour of iron alloyed with higher proportions of nickel led F. Osmond, F. Osmond and G. Cartaud, and W. Guertler and G. Tammann to assume that γ-iron and β-nickel form isomorphous mixtures—*vide infra*, iron-nickel alloys. The magnetic change is often regarded as an allotropic change, but E. C. Bain, and F. Wever found that the space-lattice of nickel at 500° is the same as it is at ordinary temp., and therefore the magnetic change is not due to a rearrangement of the atoms. J. Hopkinson found that an impure sample becomes non-magnetic at 310°, and H. E. J. T. du Bois found 300° for another impure sample. J. M. Gaugain gave 350° for the transition temperature; and, for nickel free from cobalt, of a high degree of chemical purity, and melted in hydrogen, H. Copaux obtained 340°. The point is depressed by the presence of impurities. Various observations, with more or less pure samples, were made by W. Guertler and G. Tammann, 325°; J. Hopkinson, 310°; T. P. Harrison, 374°; P. Curie, 340°; H. Pécheux, 335° to 345°; I. I. Schukoff, and H. le Chatelier, 340°; E. Jänecke, 347° to 360°; P. Weiss and R. Forrer, 357°; P. Weiss and co-workers, 363°; A. Krupkowsky, 368·3°; H. Masumoto, 376°; H. Copaux, 340°; B. Stark and D. Tararczenko, 370°; D. and H. E. Hanson, 348° and 393° respectively obtained from the cooling and heating curves; A. L. Baikoff, 360·80°; K. Honda, 348° to 351°; K. Honda and H. Takagi, 370°; L. Tieri, 355°; W. F. Colby, 280° to 310° for commercial nickel, and 370° to 380° for electrolytic nickel; M. Werner, 352°; R. L. Sanford, and L. Jordan and W. H. Swanger, 370° to 380°, for 99·94 per cent. nickel; J. Dorfman and R. Jaanus, 356·5° to 359·5°; B. V. Hill, 355° for hard nickel, and 340° for annealed nickel; and M. Werner obtained by different methods values ranging from 352° to 360°.

W. del Regno said that the transformation takes place over a range of temp. of 100° between 300° and 400°, M. F. Angell observed that the magnetic transformation temp. of nickel carbide shifted 130° by heat treatment; annealing from high temp. gives a low value, and abrupt cooling produced a value as high as 420°. J. Hopkinson observed no trace of the phenomenon of recalescence as nickel changes from the non-magnetic to the magnetic state in cooling past 310°, but A. L. Baikoff observed a slight break in the differential cooling curve at 360° in agreement with the magnetic transformation of the metal. M. Garvin and A. M. Portevin also studied the cooling curves of nickel. H. C. Cross observed a break in the heating curve of 99·94 per cent. nickel beginning at 351° to 353°, and ending at 357° to 359°; and in the cooling curve beginning at 332° and 351°, and ending at 316° and 342°. There is therefore a thermal transformation at about 350°. A. Perrier and F. Wolfers observed kinks in the heating curve of nickel at 480° and 880°. Observations were also made by M. Faraday, S. Bidwell, A. Heydweiller, C. Drucker, A. Schulze, C. H. M. Jenkins and M. L. V. Gayler, R. Ruer and co-workers, H. A. Rowland and L. Bell, J. A. Ewing and G. C. Cowan, and K. Honda and

S. Shimizu. Lord Kelvin discussed the bearing of the phenomenon on the law of the transformation of energy—*vide* iron. A change at about 700° was observed by C. Tomlinson, T. P. Harrison, W. Schlett, I. I. Schukoff, E. J. Janitzky, M. Werner, E. Cohen, E. Jänecke, and P. N. Laschtschenko. According to M. Copisarow, the change variously reported to occur between 345° and 365° is the Curie point which he represents by $\beta \rightleftharpoons \gamma$; and that which occurs at about 700° corresponds with the $\gamma \rightleftharpoons \delta$ change in iron. If the A_2-arrest is the Curie point of iron the change at about 350° is to be represented as $\alpha \rightleftharpoons \beta$ change; and the second will be equivalent to the $\beta \rightleftharpoons \gamma$ change of iron. C. L. Utterback observed a break in the total radiation of nickel between 1127° and 1170°, indicating some kind of allotropic or internal change.

F. Wüst and co-workers [9] gave 56·1 cals. per gram, or 3·29 Cals. per gram-atom for the latent **heat of fusion** of nickel at 1451°; W. P. White gave 73 cals. per gram, or 4·3 Cals. per gram-atom. J. W. Richards calculated 68 cals. per gram, and P. W. Robertson, 73 cals. per gram, for the latent heat of fusion of nickel. S. Umino gave 70·40 cals. per gram for the latent heat of fusion of nickel. The subject was discussed by E. Kordes, and N. von Raschevsky; and the relation between the heat of fusion and the vibration frequency, by W. Herz. N. F. Mott studied the relation between the latent heat, the m.p., and the electric conductivity. H. A. Jones and co-workers calculated the latent **heat of vaporization** at about 1000° to be 89,440 cals. per gram-atom; or $L_0T^{-1}=40·218-0·971 \log_{10} T -4·577 \log_{10} m-0·00206T-400T^{-1}$. E. Rabinowitsch and E. Thilo gave 0·14 volt for the heat of fusion, 3·80 volt for the heat of vaporization, and 3·94 volt for the heat of sublimation when 1 volt is 23 Cals. C. Zengelis detected no volatilization at ordinary temp.

M. Werner [10] found the **heat of the magnetic transformation** to be about 0·013 cal. per gram at 352°; S. Umino gave 2·01 cals. per gram; P. N. Laschtschenko, 3·11 cals. per gram-atom; and F. Wüst and co-workers, 1·33 cals. per gram at 320°. J. W. Richards estimated that 4·64 cals. per kilogram are absorbed by nickel at 230° and 400°. I. I. Schukoff studied the subject. J. Thomsen found the **heat of dissolution** of nickel in sulphuric acid $(Ni,H_2SO_4,aq.)=26·11$ Cals., in hydrochloric acid $(Co,2HCl,aq.)=22·58$ Cals. W. G. Mixter found the **heat of oxidation** $(Ni,\frac{1}{2}O_2)=57·9$ Cals.; W. A. Roth gave 58·45 Cals.; G. Chaudron, 57·1 Cals.; and O. Ruff and E. Gersten gave 51·5 Cals. O. Ruff and E. Gersten gave for $3Ni+C_{graphite}=Ni_3C-394$ Cals., and W. A. Roth, -10 Cals. E. D. Eastman, and G. N. Lewis and co-workers calculated 7·2 Cals. per degree at 25° for the **entropy** of nickel. W. M. Latimer, B. Bruzs, K. K. Kelley, R. D. Kleeman, and W. Herz studied this subject. E. Kordes gave 2·2 for the change of entropy in melting the metal. R. von Dallwitz-Wegner discussed the **free energy.**

The **index of refraction,** μ; the extinction coeff., k; and the **reflecting power,** R, of electrolytic nickel were measured by R. S. Minor,[11] F. Rother and K. Lauch, K. Lauch, H. Hauschild, A. de Gramont, M. Luckiesh, R. Hamer, I. C. Gardner, A. Kundt, M. Laue and F. F. Martens, P. Bergman and W. Guertler, F. Hlucka, A. Q. Tool, H. du Bois and H. Rubens, A. Pflüger, W. Rathenau, and E. Hagen and H. Rubens. The results of W. Meier for wave-lengths $\lambda=589$ to 668, for electrolytic nickel, and of G. Pfestorf for $\lambda=578$ to 254, are:

λ .	668	589	578	436	406	366	313	254
μ .	1·74	1·58	1·63	1·42	1·36	1·33	1·35	1·14
k .	3·80	3·42	2·10	1·94	1·80	1·69	1·49	1·69
R .	68·3	65·5	65·0	54·0	53·0	49·1	43·5	44·9 per cent.

The observations of G. Quincke for λ up to 527, 589, and 656, and of P. Drude for $\lambda=589$ and 630, and of M. Laue and F. F. Martens for $\lambda=630$:

λ .	431	486	527	589	589	630	630	656
μ .	1·40	1·54	1·63	1·74	1·79	1·89	1·99	1·93
k .	2·49	2·90	3·11	3·39	3·32	3·55	3·95	3·83
R .	53·3	58·6	64·5	63·4	62·0	63·7	67·6	66·8 per cent.

Observations were also made by H. von Wartenberg, M. Luckiesh, G. Pfestorf, P. R. Gleason, F. Henning, L. R. Ingersoll, C. Zakrewsky, and A. Q. Tool. I. C. Gardner studied the reflecting power in the ultra-violet; E. Hagen and H. Rubens, the variation of the emissive power with temp.; and E. Hagen and H. Rubens found for the reflecting power:

	Ultra-violet			Visible			Ultra-red		
λ .	251	326	385	420	550	770	800	5000	14,000
R .	37·8	40·3	47·8	51·9	62·6	68·8	69·6	94·4	97·2 per cent.

W. W. Coblentz and R. Stair found the reflecting power of chromium to be greater than that of nickel; and their results are summarized in Fig. 23. The reflecting power of nickel in the ultra-violet was studied by R. Hamer. H. N. Edwards measured the total reflection of nickel films; H. Hauschild, C. A. Skinner and A. Q. Tool, and K. Kiessig, the optical properties of thin films of nickel. W. del Regno observed a break in the emissivity curve near 400°. L. Tronstad, A. H. Pfund, and E. Rupp studied the optical properties of nickel.

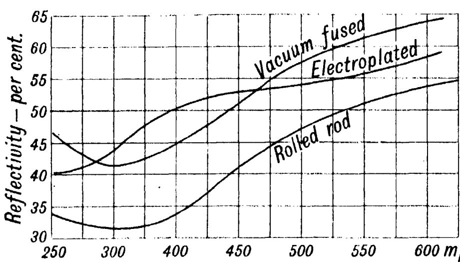


FIG. 23.—The Reflecting Power of Nickel.

J. H. Gladstone[12] gave for the **refraction equivalent** 10·4, and for the sp. refraction, 0·177. W. J. Pope gave 12·84 for the refraction equivalent of nickel. H. Knoblauch gave 77·50 for the **polarization angle** for the ultra-red heat rays, and 70·00 for yellow light. C. J. Davisson and L. H. Germer studied the polarization of the reflected electron waves; W. Lobach, and A. Kundt, the electromagnetic rotation of the plane of polarized light; and L. R. Ingersoll, H. E. J. G. du Bois, J. G. Leathem, K. H. von Klitzing, A. Pietzcker, C. J. Gorter, E. Hirsch, W. Lobach, P. D. Foote, and C. Snow, the **Kerr effect.**

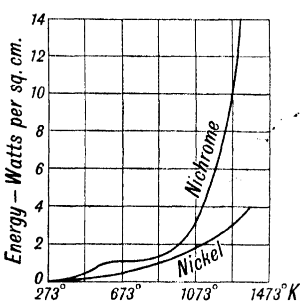


FIG. 24.—The Radiant Energy of Nickel and Nichrome.

V. A. Suydam[13] found that the total **radiation energy,** E, from heated nickel wires between 463° K. and 1283° K. can be represented by $E=cT^n$, where c, and n are constants, and T denotes the absolute temp. V. A. Suydam's value for n is 4·648 between 463° K. and 1283° K. W. del Regno gave $n=4{\cdot}588$; and M. Kahanowicz found $n=5{\cdot}5$ between 273° K. and 903° K. The subject was studied by H. Schmidt and E. Furthmann, A. G. Worthing, W. Geiss, A. L. Helfgott, and G. R. Greenslade. V. A. Suydam's values are plotted in Fig. 24 for 0·0002 mm. press. The temp. is expressed in °K., and the energy, E, in watts per sq. cm.:

	463°	603°	661°	773°	883°	951°	1071°	1181°	1283° K.
E .	0·0258	0·1000	0·1526	0·2408	0·4498	0·7012	1·2553	1·9324	2·9572

B. T. Barnes obtained for the total emissivity of soot-covered nickel:

	400°	600°	700°	800°	900°	1000°	1100°	1200°	1300°	1400°
Sooty .	0·096	0·59	1·09	1·87	3·0	4·8	7·2	—	—	—
Polished .	0·0092	0·079	0·166	0·310	0·55	0·91	1·44	2·17	3·17	4·49

C. L. Utterbach obtained for nickel $E=c_1T^{5\cdot29}$ for temp. between 650° K. and 1400° K., and $E=c_2T^{4\cdot75}$, between 1450° K. and 1600° K. There is a break in the value for nickel at about 1450°. C. Hurst, and A. G. Worthing also studied the spectral emissivity of nickel; J. K. Roberts, the energy between the atoms of

helium and the surface of nickel; H. B. Wahlin, the emission of positive ions by heated nickel; and N. C. Beese, R. S. Bartlett, G. W. Fox and R. M. Bowie, M. Benjamin, and B. J. Thomson, the thermionic emission from wires coated with barium oxide. C. J. Davisson and L. H. Germer observed a discontinuity near 1·3 A., for the electron waves from nickel.

Nickel salts furnish no distinctive **flame spectrum,** but J. N. Lockyer and W. C. Roberts-Austen,[14] J. N. Lockyer, W. N. Hartley and H. W. Moss, P. G. Hartog, C. de Watteville, and H. Auerbach studied the flame spectra in the oxy-hydrogen flame; A. K. Russanoff, the spectrum in the acetylene flame; A. G. Gaydon and R. W. B. Pearse, the flame spectrum of nickel hydride, and nickel carbonyl; F. Warbel, the quantitative analysis of nickel alloys; and G. D. Liveing and J. Dewar, the spectrum obtained during gas explosions. It is possible with the aid of the electric spark to obtain the **spark spectrum** where the more salient lines are: 5716 in the yellow; 5477 (α, Fig. 25), 5156, 5143, 5115(η), 5100, 5081(β)

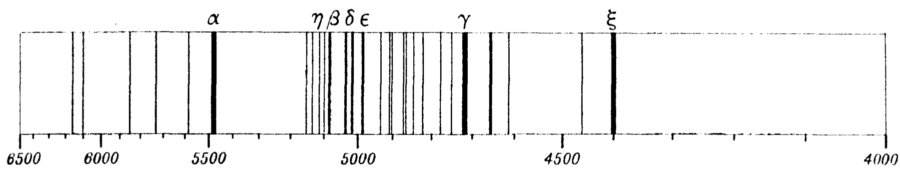


FIG. 25.—The Spark Spectrum of Nickel.

the double δ-line 5035 and 5017, 4983(ϵ), and 4936 in the green; 4905, 4866, 4715(γ), 4647, and 4606 in the blue; and 4461, and 4401(ζ) in the indigo-blue. Numerous other lines are developed by stronger sparks. Observations on the spark spectrum of nickel were first made by G. Kirchhoff, and afterwards by W. A. Miller, R. Thalén, A. J. Angström, J. N. Lockyer, L. de Boisbaudran, J. R. Capron, G. Ciamician, J. Parry and A. E. Tucker, A. Cornu, W. N. Hartley and H. W. Moss, E. O. Hulburt, W. Kraemer, H. Nagaoka and co-workers, B. de la Roche, H. Slevogt, H. N. Russell, W. G. Duffield, F. Müller, A. G. Worthing and R. Rudy, L. and E. Bloch, A. G. Shenstone, G. D. Liveing and J. Dewar, W. J. Humphreys, G. E. Hale and W. S. Adams, J. H. Pollock and A. G. G. Leonhard, F. McClean, J. M. Eder, J. M. Eder and E. Valenta, H. A. Rowland, J. Formanek, A. T. Globe, F. Müller, R. J. Lang, E. Demarçay, F. Exner and E. Haschek, W. E. Adeney, G. A. Hemsalech, O. Lohse, H. M. Reese, A. Hagenbach and H. Konen, H. Finger, and C. E. Gissing. A. W. Smith and M. Muskat, W. H. Fulweiler and J. Barnes, and E. O. Hulburt studied the spark spectrum in water.

The **arc spectrum** was examined by A. Cornu, G. D. Liveing and J. Dewar, E. Hasselberg, F. Exner and E. Haschek, L. Stütting, H. N. Russell, J. M. Eder and E. Valenta, Lord Blythwood and W. A. Scobie, S. Hamm, R. J. Lang, S. P. de Rubies, A. Sellerio, J. Holtsmark and B. Trumpy, H. Slevogt, C. C. Kiess, H. H. Marvin and A. E. Baragar, P. Mesnage, K. Bechert and L. A. Sommer, W. G. Duffield, L. Stütting, and A. C. Menzies. The effect of *pressure* was studied by W. J. Humphreys, W. G. Duffield, E. G. Bilham, and B. T. Barnes; the *ultimate rays*, by A. de Gramont; the *enhanced lines*, by J. N. Lockyer, F. E. Baxandall, and H. M. Reese; *self-induction*, by G. A. Hemsalech, B. Huber, and P. Joye; *anomalous dispersion*, by G. Geisler; the effect of *pressure*, by B. T. Barnes; the **Zeeman effect,** by H. H. Marvin and A. E. Baragar, I. M. Graftdyk, W. Arkadieff, C. J. Bakker, H. M. Reese, N. A. Kent, C. Peterke, H. Nagaoka and co-workers, C. Wali-Mohammad, K. Yamada, and J. H. van Vleck and A. Frank; the **Stark effect,** by H. Nagaoka and Y. Sugiura, E. V. Condon, T. Takamine, and H. Lowery; H. Israél, the magnetic spectrum with short Hertzian waves, and the *electrode luminescence* in electrolysis, by W. von Bolton. The **ultra-violet spectrum** was examined by G. D. Liveing and J. Dewar, R. G. zu Dohna, A. Cornu, J. C. McLennan and A. B. McLay, R. A. Millikan and co-workers, L. and E. Bloch,

R. J. Lang, V. Schumann, J. M. Eder, J. M. Eder and E. Valenta, F. Exner and E. Haschek, etc.; and the spectrum of electrically-exploded wire, by S. Smith, and R. Déchêne; and the **ultra-red spectrum,** by H. Becquerel, H. M. Randall and E. F. Barker, W. W. Coblentz, and W. F. Meggers and C. C. Kiess. The qualitative or quantitative chemical analysis by the spectrum was investigated by A. de Gramont, F. Twyman and A. Harvey, J. Parry and A. E. Tucker, A. Schleicher, F. Twyman and C. S. Hitchin, C. G. Fink and F. A. Rohrman, and J. H. Pollock and A. G. G. Leonard. The **absorption spectrum** of the vapour was examined by J. N. Lockyer and W. C. Roberts-Austen, E. von Angerer and G. Joos, W. F. Meggers, A. T. Williams, A. L. Narayan, R. G. Loyarte and A. T. Williams, and A. T. Williams; an under-water spark spectrum, by K. Majumdar, A. L. Narayan and K. R. Rao, W. F. Meggers and F. M. Walters, M. C. W. Buffam and H. J. C. Ireton, S. P. de Rubies, A. W. Smith and M. Muskat, A. C. Menzies, R. J. Lang, A. S. King, and S. Hamm; nickel hydride, by E. Olsson; and the explosive spectrum, by H. Nagaoka and co-workers. The **structure of the line spectrum** was discussed by C. C. Kiess and O. Laporte, O. Laporte, J. Veldkamp, F. M. Walters, K. Bechert, W. M. Cady, W. G. Duffield, K. Bechert and co-workers, C. R. Davidson and F. J. M. Stratton, H. H. Marvin, J. E. Mack, R. A. Merrill, A. G. Shenstone, L. S. Ornstein and T. Bouma, F. Hund, H. N. Russell, M. Kimura and G. Nakamura, W. A. M. Dekkers and A. A. Kruithof, M. Sawada, A. L. Narayan and K. R. Rao, R. J. Lang, H. Purks, R. G. Loyarte andA. T. Williams, A. C. Menzies, A. L. Narayan, P. G. Nutting, L. Janicki, C. Wali-Mohammad, and J. E. Paulson, but no **series spectra** have been detected.

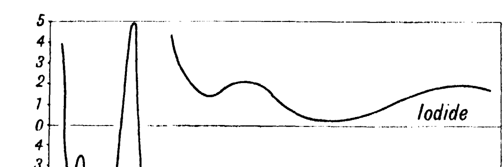


FIG. 26.—The Absorption Spectra of Aqueous Solutions of Nickel Salt.

For the colour of nickel, *vide supra.* The **absorption spectra** of green conc. aq. soln. of nickel salts shows continuous absorption bands at the violet and red ends, whilst dil. soln. of the chloride, sulphate, and nitrate show a feeble absorption band at 6563 which is characteristic. Observations on the absorption spectra of aqueous, alcoholic, or acetone soln. of nickel salts were made by D. Brewster,[15] H. Becquerel, V. Agafanoff, H. Emsmann, M. Pavlik, W. N. Hartley, J. M. Hiebendaal, T. Inoue, C. Kubierschky, H. Ley, E. Müller, J. L. Soret, J. Moir, J. von Koczkas, Y. Shibata and K. Matsuno, R. Samuel and co-workers, M. Kahanowicz and P. Orecchioni, J. Gielessen, J. C. McLennan and co-workers, N. S. Kurnakoff, T. Dreisch, J. Angerstein, H. W. Vogel, M. Kimura and M. Takewaki, R. A. Houstoun and co-workers, H. C. Jones and J. A. Anderson, and J. Formanek. The colour of nickel was discussed by J. Piccard and E. Thomas. The mol. extinction coeff., A, is a function of wave-length, λ, as indicated by R. A. Houstoun, whose results for aq. soln. are summarized in Fig. 26—*vide* the absorption spectra of cobalt salts. The effect of concentration on the mol. extinction

coeff. of aq. soln. of nickel chloride is summarized in Fig. 27. The three aq. soln. have the respective concentrations 0·10, 1·00, and 4·00 mols. per litre; and the alcoholic soln. has the concentration 0·026 mol per litre. Nickel chloride in a conc. hydrochloric acid soln. is yellowish-green. The soln. absorbs feebly in the red

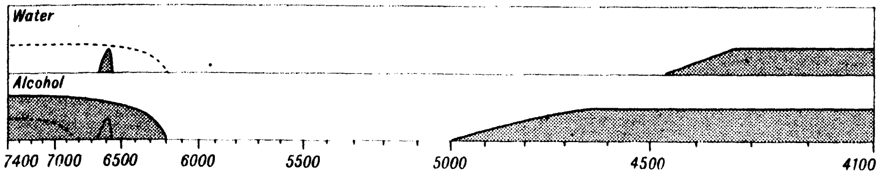


FIG. 27 and 28.—The Absorption Spectra of Aqueous and Alcoholic Solutions of Nickel Salts.

and strongly in the blue and violet. By diluting the soln., no absorption bands appear, but the continuous absorption in the red and violet becomes weaker. Ammoniacal soln. of nickel salts have a broad absorption band in the yellow at about 5740. Alcoholic soln. of nickel salts are green, and the conc. soln. have a strong absorption band in the red and violet. If the soln. be diluted with alcohol, the absorption is weaker, and besides a continuous absorption in the red and violet there is a weak band at 6607. R. A. Houstoun and A. H. Gray found for the mol. extinction coeff. of alcoholic soln. of nickel salts the results summarized in Fig. 30; and for acetone soln., the results indicated in Fig. 31.

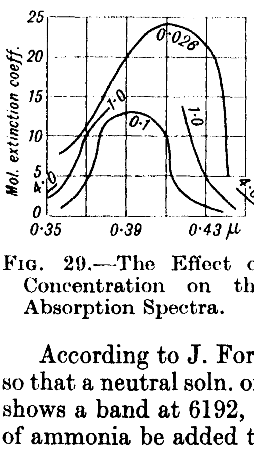


FIG. 29.—The Effect of Concentration on the Absorption Spectra.

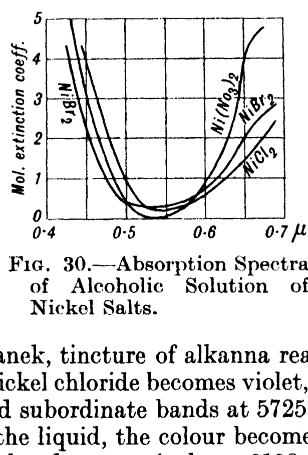


FIG. 30.—Absorption Spectra of Alcoholic Solution of Nickel Salts.

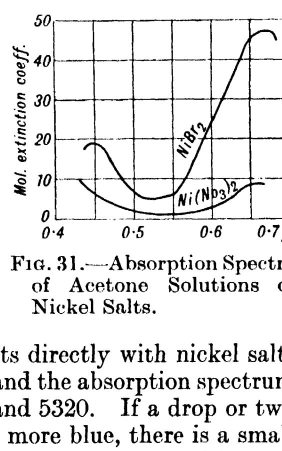


FIG. 31.—Absorption Spectra of Acetone Solutions of Nickel Salts.

According to J. Formanek, tincture of alkanna reacts directly with nickel salts so that a neutral soln. of nickel chloride becomes violet, and the absorption spectrum shows a band at 6192, and subordinate bands at 5725 and 5320. If a drop or two of ammonia be added to the liquid, the colour becomes more blue, there is a small displacement of the three bands respectively to 6198, 5732, and 5325; with more ammonia, a blue precipitate appears. Similar results were obtained with a soln. of the nitrate. M. Luckiesh, D. Starkie and W. E. S. Turner, T. Dreisch, R. W. Wood, H. P. Gage and W. C. Taylor, and P. Gilard and P. Swings studied the spectral transmission of glasses coloured with nickel.

The **X-ray spectrum** of nickel was examined by S. K. Allison,[16] A. Arends, M. Balderston, A. H. Barnes, D. K. Berkey, H. Beuthe, S. Bhargava and J. B. Mukherjee, S. Björck, H. Bohlin, D. M. Bose, G. B. Deodhar, V. Dolejsek and K. Pestrecoff, R. W. Drier, W. Duane and co-workers, S. Erikson, P. Günther and I. N. Stransky, E. Hjalmar, M. Ishino and K. Kojima, S. Kawata, B. Kievit and G. A. Lindsay, A. I. Krasnikoff, K. Lang, A. Leide, A. E. Lindh, L. H. Martin, H. G. J. Moseley, B. C. Mukherjee and B. B. Ray, G. Ortner, J. Palacios and N. Velasco, L. G. Parratt, S. Pastorello, M. Privault, H. Purks, W. F. Rawlinson, B. B. Ray and co-workers, H. S. Read, O. W. Richardson and co-workers, F. K. Richtmyer and E. Ramberg, N. Seljakoff and co-workers, J. Shearer, M. Siegbahn and co-workers, N. Stensson, C. H. Thomas, R. Thoraeus, J. Valasek,

J. H. Williams, Y. H. Woo, R. W. G. Wyckoff, and S. Yoshida, who observed for the K-series, $\alpha_2\alpha'=1\cdot65860$; $\alpha_1\alpha=1\cdot65467$; $\alpha_3\alpha_4=1\cdot6476$; $\beta_1\beta=1\cdot49669$; and $\beta_2\gamma=1\cdot48403$, with the absorption limits 1·4890. M. Siegbahn and R. Thoraeus, B. C. Mukherjee and B. B. Ray, S. Björck, J. H. van der Tuuk, J. Shearer, W. Stenström, H. Hirata, S. Kawata, M. Levi, C. E. Howe, F. C. Chalkin, and G. Kellström studied the L-series; and B. C. Mukherjee and B. B. Ray, E. C. Stoner, R. B. Witmer and J. M. Cork, S. Björck, N. Bohr and D. Coster, B. Walter, M. Levi, and S. R. Rao, the M-series.

W. M. Coates,[17] and O. W. Richardson and co-workers studied the emission of **X-rays**; N. Ahmad, S. J. M. Allen, L. M. Alexander, T. E. Aurén, M. Balderston, C. G. Barkla and co-workers, L. L. Barnes, J. A. Bearden, J. A. Becker, W. H. Bragg and H. L. Porter, A. Hébert and G. Reynaud, R. A. Houstoun, G. W. C. Kaye, H. Kiessig, P. G. Kruger and W. E. Shoupp, L. H. Martin and K. C. Lang, J. Palacios and M. Velasco, L. G. Parratt, J. A. Prins, S. R. Rao, B. B. Ray and R. C. Mazumdar, H. S. Read, and F. K. Richtmyer and co-workers, the absorption of X-rays; K. Grosskurth, and J. A. Becker studied the effect of a magnetic field on the absorption of X-rays; G. W. Brindley and F. Spiers, D. E. Lea, and D. Blochinzeff and F. Halperin, the scattering of X-rays; H. E. Stauss, the reflection of X-rays; A. J. Lamaris and J. A. Prins, and I. Umansky and V. Veksler, the dispersion of X-rays; J. Veldkamp, the effect of the lattice on the structure of the X-ray absorption spectrum; H. Kiessig, the interference of X-rays by thin films; S. Bhargava and J. B. Mukherjee, the changes produced in X-rays by their passage through thin films of nickel; S. R. Rao, the excitation of X-rays from the different faces of a crystal; C. T. Chu, F. C. Chalkin, E. Vette, S. R. Rao, and O. W. Richardson and S. R. Rao, the excitation of soft X-rays from single crystals and polycrystalline nickel; A. H. Compton, O. W. Richardson and F. S. Robertson, L. P. Davies, and U. Nakaya, the effect of oxidation on the emission of X-rays by nickel. H. S. Read studied the effect of temperature; and J. A. Becker, the slight effect of a magnetic field of 18,000 gauss on the absorption coeff. of nickel for X-rays of short wave-length; R. W. G. Wyckoff, H. Kiessig, R. Piedmiller, and H. W. Edwards, the reflection of X-rays from nickel; W. A. Wood, G. I. Finch and A. G. Quarrell, the diffraction; L. T. Pockman and co-workers, the intensities; E. Acends, the fluorescent effects; H. Kulenkampff, and F. K. Richtmyer and L. S. Taylor, the intensity of X-rays from nickel; S. Pastorello, nickel as a deflection lattice for X-rays; C. D. Cooksey, the radiation produced by X-rays. According to R. W. Jones and G. W. Brindley, B. B. Ray, and R. W. G. Wyckoff, the atomic scattering of X-rays is a minimum at the K-absorption limit of nickel, and a maximum near its resonance wave-length; H. Möller found that the K-doublets are split into two components by straining the metal. N. H. Moxnes, and P. Günther and I. N. Stransky studied the analysis of alloys of nickel and cobalt; E. Wainer, mixtures with ferric oxide, and with calcium oxide; and W. Arkadieff, the magnetic spectrum of the Hertzian waves.

A. T. Waterman, H. Schenck, C. Davisson and C. H. Kunsman, K. Hayakawa, S. R. Rao, H. Schenck, H. Nukiyama and H. Horikawa, H. E. Farnsworth, A. L. Patterson, E. W. B. Gill, R. M. Chaudhri, R. L. Petry, W. Espe, and P. Tartakovsky and V. Kudrjavzeva studied the emission of **electrons** by nickel; H. A. Barton, the emission of electrons from oxide-coated filaments; E. F. Richter, the emission from films coated with barium oxide; W. Distler and G. Mönch, the potential of electronic emission from glowing nickel; G. Glockler, electron affinities; W. Uyterhöven and M. C. Harrington, H. A. Erikson, C. Hurst, S. R. Rao, G. Shearer, and M. L. E. Oliphant and P. B. Moon, the liberation of electrons by positive ions; H. B. Wahlin, the emission of electrons from hot wires; R. Viohl, the heat of condensation of electrons on nickel; C. H. Thomas, A. L. Klein, M. C. Harrington, S. R. Rao, M. N. Davis, B. J. Thomson, W. S. Stein, S. R. Rao, H. Nukiyama and H. Horikawa, K. S. Woodcock, P. B. Moon, P. Tartakovsky and V. Kudrjavzeva, R. M. Chaudhri, W. Uyterhöven and M. C. Harrington, N. C. Beese,

W. J. Jackson, and M. L. E. Oliphant, the secondary emission of electrons from nickel bombarded by positive rays; L. H. Germer, H. Raether, C. Davisson and L. H. Germer, K. L. Horovitz and co-workers, T. Benecke, and E. Rupp, the diffraction of electrons by nickel; H. E. Farnsworth, C. Davisson and co-workers, R. W. G. Wyckoff, A. L. Patterson, and R. L. Doan, the scattering of electrons; L. H. Germer, H. W. Edwards, and E. Rupp, the reflection of electrons; C. Boeckner, the radiations emitted by bombardment with slow electrons; O. Klemperer, electronic collisions; E. Rupp, C. Davisson and co-workers, the absorption of electrons; C. Davisson and L. H. Germer, the anomalous dispersion at 1·3 A. of electron waves by nickel; C. Davisson and L. H. Germer, the refraction of electrons; G. W. Fox and R. M. Bowie, and H. E. Farnsworth, and D. A. Wells, the energy of distribution of secondary electrons; and E. D. Eastman, the thermal capacity of the electrons; L. H. Germer, the electronic motions and gas absorption; R. Ruedy, the free and bound electrons in nickel; D. A. Wells, the energy of the emission; and W. Distler and G. Mönch, the thermionic work function.

L. L. Barnes studied the emission of **positive ions** from nickel; A. K. Brewer, the effect of ammonia on the emission of positive ions; H. R. von Traubenberg, the range of the α-particles in nickel; and K. S. Woodcock, the emission of electrons from nickel bombarded by α-rays. J. K. Roberts studied the exchange of energy between **helium atoms** and a nickel surface; P. B. Moon, the emission of electrons from nickel bombarded by **cæsium ions**; R. B. Sawyer, and A. Longacre, the reflection and scattering of **lithium ions** from nickel crystals; and A. Coehn and K. Sperling, the action on a photographic plate. W. G. Guy observed no radioactivity with nickel.

R. D. Kleeman found the ionization produced by the α-, β-, and γ-**rays** to be in the proportion 1·72 : 2·67 : 2·81. H. Pattersson studied the reflection of α-particles from atomic nuclei; and E. Rie, the penetration of **radium rays.** G. P. Thomson studied the diffraction of the **cathode rays** by nickel; J. A. Becker, the loss in intensity on transmitting slow cathode rays through nickel films of thickness $0{\cdot}02\mu$ and $0{\cdot}04\mu\mu$, at 20 volts—it amounts to $1{\cdot}12\times10^{-4}$, and $0{\cdot}047\times10^{-4}$, respectively; and G. Fournier, the absorption of β-rays. E. Rie observed that the depth of penetration of radioactive recoil atoms from radium emanations is $10\mu\mu$. I. Curie and F. Joliot, E. Fermi and co-workers, and W. G. Guy studied the induced radioactivity of nickel. W. Arkadieff studied the **electric and magnetic spectra** of electro-magnetic waves; and Y. H. Woo, the **Compton effect.** A. Imhof showed that stationary waves are emitted by wires heated by an alternating current.

N. Piltschikoff said that nickel emits **Moser rays** capable of passing through paper, celluloid, or aluminium, and of decomposing silver bromide. E. Amaldi and co-workers observed no induced radioactivity with nickel. R. Robl observed no luminescence with nickel in **ultra-violet light.**

The **photoelectric effect** was investigated by L. P. Davies,[18] J. F. Chittum, J. S. Hunter, R. Hamer, R. B. Jones, H. Klumb, J. R. Nillson, T. Pavolini, G. Reboul, S. C. Roy, F. Hlucka, W. Klug, J. Chadwick and M. Goldhaber, A. G. Shenstone, J. J. Weigle, and G. B. Welch. S. Werner gave 2850 A. for the photoelectric threshold corresponding with the limiting frequency of the photoelectric effect; R. Hamer gave 3050 A.; G. B. Welch, 3050 A.; and J. J. Weigle, 3540 A. The subject was studied by J. H. Wolfenden, C. Kenty, P. Lukirsky and S. Prilezaeff, U. Nakaya, F. Hlucka, G. B. Bandopadhyaya, G. N. Glasoe, O. Koppius, and F. G. Tucker. H. Klumb, O. I. Leypunsky, and W. Frese investigated the influence of occluded gas on the photoelectric effect; and R. F. Hanstock, the effect of polishing the metal. H. S. Allen, and W. Frese found that the oxidizing agents which make nickel passive are those which reduce the photoelectric sensitiveness. F. Ehrenhaft found that powdered nickel exhibited positive and negative **photophoresis,** or movement with or against the direction of a beam of incident light.

H. N. Russell [19] gave 7·64 and 18·2 volts for the **ionization potentials** of nickel, and the subject was studied by C. T. Chu, B. B. Ray and R. C. Mazumdar, S. C. Biswas, A. C. Davies and F. Horton, U. Andrewes and co-workers, R. L. Petry, G. B. Welch, G. B. Kistiakowsky, and C. H. Thomas. H. Wahlin found the **critical potentials** in nickel vapour between 0 and 17 volts; and O. W. Richardson and co-workers represented the series by $v=181\cdot9-2357n^2$, where $n=4$, 5, 6, 7, 8, 9, 10, 11, and 12 volts. C. H. Thomas gave for the L-series of nickel, 833·4 and 948 volts. W. Herz gave for the **vibration frequency** of nickel $8\cdot07\times10^{12}$. The subject was studied by W. Herz, J. B. Austin, J. E. P. Wagstaff, and G. B. Kistiakowsky.

A. Matthiessen and C. Vogt [20] found that the **electrical conductivity** of what was thought to be pure nickel was 13·106 on the assumption that the values for silver and hard-drawn copper were respectively 100 and 99·75. L. Weiller obtained a conductivity of 7·89 (silver 100). J. Dewar and J. A. Fleming obtained $14\cdot5\times10^4$ mhos at 0° for the conductivity of nickel; L. Holborn, $15\cdot2\times10^4$ mhos; G. Niccolai, $8\cdot3\times10^4$ mhos; and W. C. Ellis and co-workers, $0\cdot966\times10^5$ mhos. J. A. Fleming calculated the **electrical resistance,** R, to be 12·357 microhms per cm. cube, but with electrolytic nickel he obtained a sp. resistance of 6·935 microhms per cm. cube at 0°. H. Masumoto gave $R=0\cdot00000858$ ohm per cm. cube for the resistance of nickel at 30°. A. Campbell reported two commercial samples with the respective resistances 8 and 12 microhms per cm. cube at 0°; H. Copaux gave 6·4 microhms; R. Ruer and K. Kaneko, 7·7 microhms; H. Pécheux—curve 3, Fig. 32, 9 microhms; P. D. Merica, 6·5 microhms; L. Jordan and W. H. Swanger, 7·236 microhms; F. Wenner and F. R. Caldwell, 7·236 microhms for annealed 99·94 per cent. nickel at 20°; and E. P. Harrison—curve 2, Fig. 32—10·288 microhms per cm. cube of purified nickel. M. F. Angell obtained between 0° and 1200° a curve resembling 2, Fig. 32. B. D. Enlund, C. M. Smith and J. C. MacGregor, J. MacGregor-Morris and R. P. Hunt, D. H. Browne and J. F. Thompson, W. Rohn, H. le Chatelier, F. H. Schofield, C. A. de Bruyn, and C. H. Lees also measured the electrical resistances of nickel. W. H. Stannard gave a table of the resistance of the metal. H. Pécheux reported four commercial samples with resistances 9, 10·24, 13·25, and 14·25 microhms per cm. cube respectively; and W. Jäger and H. Diesselhorst obtained 8·50 microhms per cm. cube at 18°, and 6·37 at 100°, with a sample containing Co, 1·4; Fe, 0·4; Mn, 1·0; and Cu, 0·1.

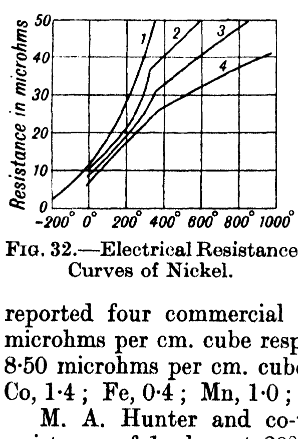


FIG. 32.—Electrical Resistance Curves of Nickel.

M. A. Hunter and co-workers' results—curve 4, Fig. 32—are based on a resistance of 1 ohm at 20°, when the actual values were respectively 64, 84, and 117 for the three grades of nickel, A, C, and D.

		20°	100°	200°	400°	600°	800°	1000°
R	A	1·000	1·43	2·06	3·52	4·15	4·73	5·38
	C	1·00	1·36	1·90	3·02	3·49	3·96	4·50
	D	1·00	1·39	1·68	2·31	2·62	2·94	3·30

The resistance decreases very much as the proportion of impurities increases. The transformation temp. for the three grades are respectively 350°, 320°, and 275°. V. A. Suydam gave for the resistance, R ohms at:

	0°	339°	352°	457°	551°	726°	980°	1000°
R	1·000	2·649	3·542	4·028	4·359	4·966	5·463	5·920

G. Niccolai gave for the ratio of the resistances at θ and 0°, $R : R_2$—curve 1, Fig. 32:

	−192°	−78°	100°	200°	300°	400°
$R : R_0$	0·173	0·600	1·683	2·537	3·559	4·770
$R : R_0$	0·114	0·581	1·666	2·511	—	—

where the data in the last line are due to L. Holborn. H. Schimank gave for the ratios at 0·09°, —78·6°, —122·6°, and —252·8°, respectively, $R : R_0$=1·0000, 0·6722, 0·2904, and 0·2046, and R_0=2·147 ohms. Observations were made by W. Giess and J. A. M. van Liempt, B. Svensson, C. Drucker, E. Horn, C. A. Hering, and K. Honda and Y. Ogura. K. Honda and T. Simidu gave for the resistance, R microhms per cm. cube:

	26°	81°	197°	310°	401°	531°	664°	764°	836°
$R \times 10^6$.	11·9	14·8	21·6	31·2	37·4	42·0	46·8	49·3	51·0

F. H. Schofield gave for the resistance, R ohms per cm. cube:

	14°	111°	142·4°	200·5°	304·1°	409·6°	519·4°	691·1°	820·7°
$R \times 10^6$.	10·04	14·60	16·17	19·73	28·15	35·00	38·65	43·60	47·60

W. Meissner and co-workers measured the resistance at temp. down to —271·8°, and he obtained for the ratio, r, of the resistance, R, at the observed temp. to the resistance, R_0, at 0°, and for the ratio, r_{red}, of the pure metal when the observed resistance at 0° is $1·80 \times 10^{-4}$ ohm:

	0·16°	−185·58°	−194·15°	−252·60°	−268·79°	−271·66°
r	1	0·1179	0·09193	0·006622	0·005078	0·005027
r_{red}	1	0·1135	0·08735	0·001610	0·000058	0·000000

J. C. McLennan and co-workers found the sp. resistance of nickel at 0° to be 6·93 and at —152·4°, 0·59. W. Meissner gave:

	0·20°	−185·57°	−194·14	−252·60°	−268·79°	−271·66°
R . .	1	0·1179	0·09193	0·06622	0·005078	0·005027

or, by extrapolation, 0·00502 at —273°. W. Tuijn and H. K. Onnes found that nickel did not show super-conductivity at low temp. J. Dewar and J. A. Fleming gave 0·00620 for the temp. coeff. of the resistance between 0° and 100°; L. Holborn, 0·00675; P. W. Bridgman, 0·00634; C. G. Fink and F. A. Rohrman, 0·0064; F. Wenner and F. R. Caldwell, 0·0067; W. Giess and J. A. M. van Liempt, 0·00667 for annealed nickel, and 0·00706 for nickel after heating 30 min. in vacuo at 1000°; and A. A. Somerville gave the results summarized in Fig. 33. C. F. Marvin found that the relation between the resistance between three samples of nickel and the temp. could be represented by log R=1·08539+0·0016990θ; log R=1·90045+0·0018188θ; and log R=0·96145+0·00145θ. J. Kramer, Y. Maslakovetz, R. C. L. Bosworth, and A. Riede measured the resistance of thin films. J. Müller studied the resistance with direct and alternating currents; and A. T. Waterman, E. W. Hall, and K. Höjendahl, the electronic theory of conductivity with respect to the nickel.

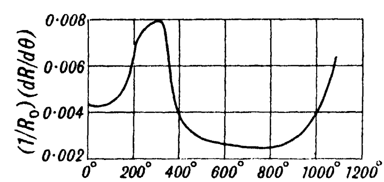


FIG. 33.—The Temperature Coefficient of the Electrical Resistance of Nickel.

C. G. Knott observed that the increase in the resistance per degree rise of temp. continues regularly up to about 200°, and it is then nearly constant up to 320°, when an abrupt change occurs, and after that there is a slow uniform rise. Thus, within 200° and 320°, the slope of the temperature-resistance curve is steeper than it is anywhere else. W. del Regno found a break in the resistance curve near 400°. A. Battelli represented the change in the resistance at θ, between 0° and 220°, to be $0·003981\theta - 0·0_5 22\theta^2$; between 230° and 360°, $0·004352\theta - 0·0_5 18\theta^2$; and between 380° and 410°, $0·003322\theta - 0·0_5 12\theta^2$, when the resistance at 0° is 2·312. M. F. Angell observed a break in the form of the curve at the magnetic transformation point, near 370°, and another break at about 700°, which was said to correspond with another allotropic change, but the critical point at 700° was not observed by K. Honda and T. Simidu. Both F. H. Schofield, and M. Tuorneur observed points of inflexion in the curve near the temp. of the magnetic trans-

formation. A. L. Williams and co-workers studied the electrical conductivity of mixtures of nickel and mica.

W. Broniewsky studied the relation between the *specific volume* and the electrical resistance. S. R. Williams and R. A. Sanderson obtained the results summarized in Fig. 34 for the change in the resistance of strips of nickel of different degrees of *hardness* in a magnetic field of 75·3 gauss.

P. W. Bridgman found that the electrical resistance of nickel is modified by *pressure* ranging from 0 to 12,000 kgrms. per sq. cm.:

	0°	25°	50°	75°	100°
Resistance . . .	1·0000	1·1108	1·2288	1·3542	1·4873
Press coeff. 0 . .	$-0·0_5 1581$	$-0·0_5 1578$	$-0·0_5 1586$	$-0·0_5 1600$	$-0·0_5 1631$
Press coeff. 12,000 .	$-0·0_5 1393$	$-0·0_5 1428$	$-0·0_5 1464$	$-0·0_5 1499$	$-0·0_5 1535$

The press. coeff. at 0° is thus $-0·0_5 158$ against the value $-0·0_5 138$ obtained by E. Lisell. P. W. Bridgman found the press. coeff. at 0°, $-78·4°$, and $-182·9°$, with 7,000 kgrms. per sq. cm., to be respectively $0·0_5 185$, $-0·0_5 20$, and $-0·0_5 188$. E. D. Williamson gave 0·9823 for the ratio of the electrical resistance with 1 kgrm. per sq. cm., and with 12,000 kgrms. per sq. cm. Observations on the effect of press. on the resistance were made by K. Honda and co-workers, S. Arzibischeff adn V. J. U. Juschakoff, A. W. Smith, A. Schulze, H. Tomlinson, W. E. Williams, M. Cantone, G. Ercolini, A. Nobile, J. B. Seth and C. Anand, R. S. Bedi, L. W. McKeehan, and F. Skaupy and O. Kantorowicz. According to S. Arzibischeff and V. J. U. Juschakoff, the resistance of a nickel wire under *tension* decreases at first, reaches a minimum at 0·05 elongation at room temp., and then increases. There are discontinuities between 343° and 360°. The inflexion point occurs at about 353°, which is near the Curie point for nickel, so that the phenomenon appears to be related with the magnetic transformation of the metal. The minimum is less pronounced at higher temp., and disappears at the critical point; beyond that, the effect of stretching is to increase the resistance almost linearly. P. W. Bridgman observed the percentage change in the electrical conductivity of nickel, in tension with a load of 1900 kgrms. per sq. cm., to be 0·48, or $0·0_5 252$ per kgrm. per sq. cm. R. S. Bedi, L. W. McKeehan, and S. Arzibischeff and V. J. U. Juschakoff studied the effect of tension. H. Tomlinson observed that the decrease in the electrical resistance per unit produced by a stress of a gram per sq. cm. is 3216×10^{-12}. F. Gredner observed that the decrease in the resistance of metal wires under tension as the temp. is raised to about 500° is quicker and greater the higher is the temp. The minimum resistance with nickel occurs at about 550°. The change is not due to a change from an amorphous to a crystalline state, but rather to the formation of spaces between the crystallites, and depends also on the gliding surfaces of the metal, as well as to the alteration under tension from an irregular to a suitably arranged system of crystallites; J. B. Seth and C. Anand noted that the resistance of a nickel wire decreased on stretching, reaching a minimum value when the extension was 15 per cent. of that of fracture, and thereafter it increased continuously. The initial part of the extension-resistance curve down to the minimum value of the resistance exhibited a hysteresis effect when the wire was subjected to a cycle of values of extension. R. S. Redi observed that the minimum attained in the resistance curve when nickel is stretched corresponds with the elastic limit.

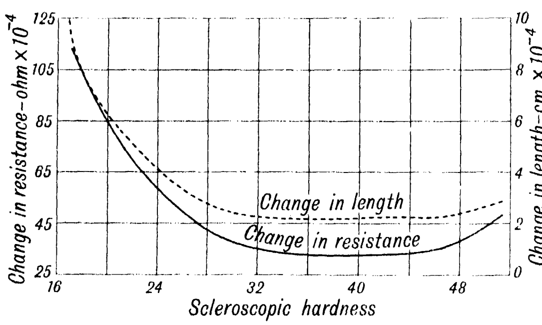


FIG. 34.—The Effect of Hardness on the Electrical Resistance and Magnetostriction of Nickel.

The preliminary stretching was not observed with copper, iron, or steel. T. Ueda studied the effect of *torsion* on the resistance of nickel; W. Brown, the effect of an electrical current on the subsidence of torsional oscillations; and H. L. Brakel, the effect of *vibration* on the resistance of nickel.

K. Honda and T. Hirone, and S. de Negri studied the effect of press. on the resistance of nickel; F. Skaupy and O. Kantorowicz, the resistance of compressed powdered nickel; O. Jaamaa and Y. E. G. Leinberg, and L. Reichardt measured the resistance of powdered nickel; and J. Kramer and H. Zahn, A. Riede, H. B. Peacock, and R. Riedmiller, the resistance of thin films of nickel. L. R. Ingersoll and J. D. Hanawalt observed that the electrical resistance, at 0° to 450°, is greater with films spluttered in argon at 0·5 mm. press. than it is with films obtained by the evaporation of nickel; and the resistance of evaporation films is greater than it is with nickel *en masse*. A. Sieverts discussed the effect of occluded gases on the conductivity of nickel; and T. Skutta observed that the resistance of nickel increases in an atm. of hydrogen and nitrogen at press. up to 30 atm. It was supposed that an unstable solid soln. of nickel and hydrogen is formed in the presence of hydrogen. The theory of the electrical conductivity was discussed by K. F. Herzfeld, K. Höjendahl, M. von Pirani and A. R. Meyer, and F. Simon.

Although M. F. Angell observed that the resistance of nickel, in the range 200° to 800°, is not changed by heat treatment, H. Wedding said that the electrical resistance of cast nickel is not changed by forging. M. Maclean found the resistance of drawn and undrawn nickel to be respectively as 0·2287 : 0·0480. H. Tomlinson obtained analogous results. P. Kapitza said that the physical changes produced in nickel by hardening and annealing have a marked effect on the electrical resistance. A. Krupkowsky gave for the resistance of quenched nickel $8{\cdot}84\times10^{-6}$, which becomes $8{\cdot}03\times10^{-6}$ when annealed; the corresponding temp. coeff. were, respectively, 0·00577 and 0·00622. L. Guillet and M. Ballay found that as a result of cold-work, the resistance of nickel was increased 2·70 per cent. G. Tammann and co-workers studied the subject.

R. Kikuchi, and H. M. Barlow compared the electrical and *thermal conductivities of nickel*; and K. Honda and T. Simidu found that the product of the sp. resistances with the thermal conductivities is not constant, but ranges between 1·58 at 26° to 4·30 at 400°. This is in agreement with observations on other ferromagnetic metals. M. F. Angell found a steady region in the value of the product kRT, with a rise of temp., and K. Honda and T. Simidu, and F. H. Schofield observed that the product tends to become constant at about 2·6 from 300° upwards. A. Eucken and K. Dittrich also studied the application of Wiedemann and Franz's rule. C. Drucker studied the relation between the *specific heat* and the electrical resistance; A. Stein, the relation between the *melting-point* and the resistance; N. F. Mott, the relation between the *latent heat* and the m.p.; and A. Farkas and H. H. Rowley, the loss of heat by heated wires. C. E. Guye and A. Schidloff estimated that the raising of the electrical resistance of nickel by an *electric field* will probably be greater than is the case with iron. R. Holm and W. Meissner studied the contact resistance of nickel.

D. Goldhammer measured the change in the electrical resistance of nickel in a *magnetic field*; L. Grunmach and F. Weidert observed a decrease of −1·4 per cent. by a field strength of 10,000 gauss, W. E. Williams gave −1·2 per cent., and G. Barlow, 1·4 per cent., whilst N. d'Agostino observed a decrease of 1·0 per cent. with a field-strength of 6000 gauss; and G. Berndt, a decrease of 0·60 per cent. with a field-strength of 3040 gauss. C. G. Knott observed that in a field of 3800 gauss, the percentage change in the resistance with rise of temp. becomes smaller up to 260°, it then passes through a minimum, and afterwards rises rapidly to a maximum at 310°, and then falls to a proportionally low value at 344°. C. G. Knott also measured the relation between the magnetization and the electrical resistance of nickel at elevated temp., and he found that when a nickel strip is conveying a current its conductivity is diminished in a longitudinal magnetic field, and increased

in a transverse magnetic field. Reversal of either magnetic field does not change the accompanying effect on the conductivity. When a cyclic longitudinal field is superposed upon a steady transverse field of magnitude less than a certain critical value, the diminution in the conductivity is less marked as the transverse field increases and practically vanishes when this critical value of transverse field is reached. When the steady transverse field exceeds this critical value the superposed cyclic longitudinal field causes an increase in the conductivity, and this increase becomes more marked as the longitudinal field is made greater. When a cyclic transverse field is superposed upon a steady longitudinal field the increase in conductivity is augmented. Not only does the increase of conductivity grow greater with the stronger transverse field but it also grows greater as the steady longitudinal field is increased. H. Tomlinson obtained similar results.

Observations on the resistance of nickel in magnetic fields were made by M. S. Alam, G. Alloco, K. Bamberger, G. Barlow, H. E. J. G. du Bois, M. Cantone, R. Dongier, A. Drigo, E. Englert, G. Fae, A. Garbasso, W. Gerlach, W. Gerlach and K. Schneidermann, T. Gnesotto, L. Grunmach and F. Weidert, M. M. S. Gupta and co-workers, C. W. Heaps, T. Hirone, W. A. Jenkins, W. M. Jones and J. E. Malam, P. Kapitza, S. Kaya, P. McCorkle, L. W. McKeehan, Y. Matuyama, M. Medici, A. Nobile, J. Obata, E. A. Owen, H. H. Potter, K. Schneiderhan, A. W. Smith, D. S. Steinberg and F. D. Miroschnitschenko, O. Stierstadt, W. Thomson (Lord Kelvin), F. Vilbig, S. R. Williams and R. A. Sanderson, and W. E. Williams.

F. C. Blake obtained the following changes of electrical resistance, δR per cent., by a transverse magnetic field of H gauss, at different temp.:

	H	−190°	−75°	0°	18°	100°	182°
δR	0	0	0	0	0	0	0
	1,000	0·20	0·23	0·07	0·7	0·96	0·04
	2,000	0·17	0·16	0·03	0·03	0·72	−0·07
	3,000	0	−0·05	−0·34	−0·36	−0·14	−0·60
	10,000	−0·18	−0·27	−0·82	−0·95	−1·23	−1·76
	14,000	−0·18	−0·32	−0·91	−1·04	−1·37	−1·95
	20,000	−0·16	−0·41	−1·03	−1·17	−1·59	−2·25
	35,000	−0·10	−0·63	−1·32	−1·50	−2·13	−2·98

C. W. Heaps represented the effect of a transverse field on the electrical resistance by Fig. 35. C. G. Knott gave for the change of resistance, δR, of 100,000 ohms of

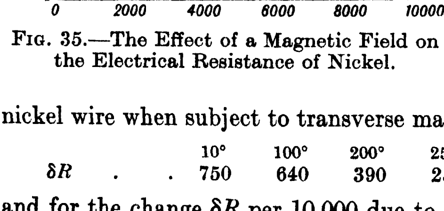


FIG. 35.—The Effect of a Magnetic Field on the Electrical Resistance of Nickel.

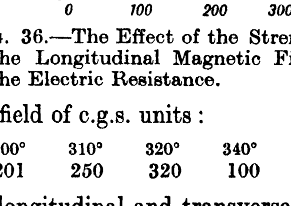


FIG. 36.—The Effect of the Strength of the Longitudinal Magnetic Field on the Electric Resistance.

nickel wire when subject to transverse magnetic field of c.g.s. units:

	10°	100°	200°	250°	300°	310°	320°	340°	350°
δR	750	640	390	250	201	250	320	100	5

and for the change δR per 10,000 due to cyclic longitudinal and transverse fields, $H=50$ c.g.s. units:

		0°	100°	200°	300°	400°	600°	800°
δR	Long.	61	27	1·8	−7·2	−11·4	−148	−15·6
	Trans.	—	−83	−142	−164	−175	−183	−185

W. Gerlach's curves for the percentage changes in the resistance of nickel as a function of the longitudinal field strength at different temp. below the Curie point, are shown in Fig. 36. These changes are approximately proportional to the

external field. The lower curves refer to the lower temp. The curves, Fig. 36, for the change in the resistance with magnetization are linear from about the beginning of the knee of magnetization up to saturation for about 20° and 200°. When the linear part of the curve is extrapolated (dotted line) to furnish a magnitude whose product by the absolute temp. is constant, the change in the resistance with field-strength represented by continuous line, Fig. 37, shows a hysteresis which is smaller than the hysteresis of magnetization represented by the dotted line, Fig. 38.

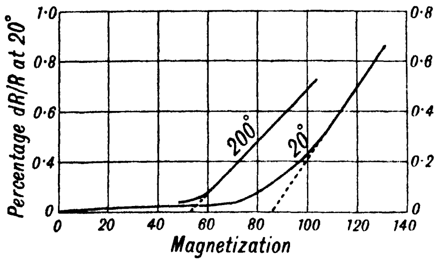


FIG. 37.—The Effect of Magnetization on the Electrical Resistance.

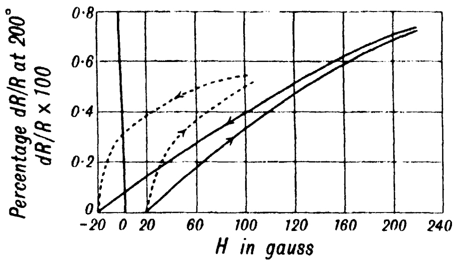


FIG. 38.—The Hysteresis of the Change in the Electrical Resistance with Magnetization.

S. Kaya found that with single crystals of nickel the longitudinal effect in every direction of the axes—tetragonal, diagonal, and trigonal—increases the resistance, and in the decreasing order (111), (110), and (100). The transverse effect gives an increase or decrease in the resistance according to the direction of the magnetic field. There is an increase with (001), and a decrease with ($\bar{1}$10) and ($\bar{1}$11). According to W. L. Webster, there is an effect with the (100) and (110) directions exactly similar to what has been found for iron (*q.v.*) for the magnetically corresponding directions, Fig. 39; but there is, in addition, a very large effect in the direction of easiest magnetization both for longitudinal and transverse phenomena. The curve for the (111) direction, where the change of resistance occurs within 5 per cent. of saturation, may be due to the acquisition, near the region of saturation, of uniformity and continuity in the magnetic direction of the crystals. This explanation involves a decrease in the resistance and not the increase actually observed. W. L. Webster continued: In the case of the transverse phenomenon, there is also a change of resistance with magnetization along the (111) axis, but in this case it is a decrease in resistance. This suggests that both the changes that were found for this direction are akin to the changes of length in the direction of easiest magnetization that occur in nickel and iron. That is, they are due to the electrical anisotropy of nickel magnetized along its magnetic axis. If this be so, then the appearance of the curve, which is not at all what would be expected on such a view, must be due to comparatively large errors in the magnetization scale—errors particularly likely to occur for the direction of easiest magnetization. The fact that the anisotropy occurs only in nickel and not in iron must be connected with the difference in the relation between the magnetic and crystallographic axes in the two metals. In the case of iron the two sets coincide, and both have the simplest symmetry possible, whereas in nickel there are four magnetic axes which do not possess the simple symmetry of the crystal structure of this metal. There may be a further cause in that in iron there are approximately three magnetic electrons per atom, all of which have not yet been shown to have that relation to conductivity which was found for the single magnetic electron of nickel. Anomalies in the resistance of nickel in a magnetic field reported by F. Vilbig, were found

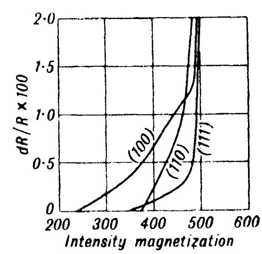


FIG. 39.—Magneto-resistance Curves for Single Crystals of Nickel.

by O. Stierstadt to be the result of errors mainly arising from incomplete demagnetization.

H. H. Potter measured the change of resistance of a nickel wire with transverse and longitudinal magnetization, and a selection of these results at different temp. is summarized in Fig. 40. The dotted curves refer to the field parallel to the current, and the continuous curves to a field perpendicular to the current. In the neighbourhood of the Curie point, the change of resistance is independent of the field, and varies with the field and temp. in a way analogous to the variation of the magneto-caloric effect—Fig. 40.

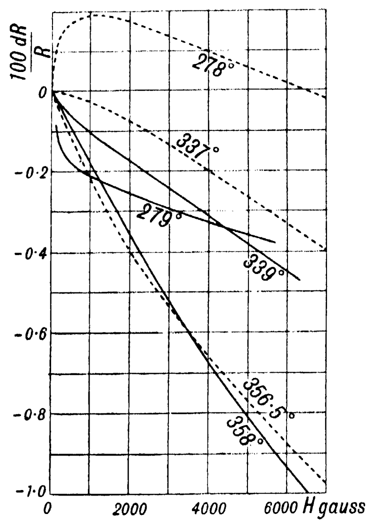


FIG. 40.—The Effect of Longitudinal (dotted) and Transverse (continuous) Fields on the Resistance.

N. Harvey [21] observed no **voltaluminescence** with nickel. R. D. Kleeman and W. Fredrickson studied the electrical charges on colloidal particles of nickel in distilled water; A. Coehn and A. Lotz, and P. E. Shaw and co-workers, the **frictional electricity** or **triboelectrical effect** of nickel against glass, etc.; W. A. Rudge, the production of electrically charged dust when nickel is spluttered in air in a brass tube; and J. B. Seth and co-workers, the e.m.f. developed when nickel and steel are in contact and in relative motion. P. A. Mainstone studied the effect of heat treatment.

W. Ende measured the gas-metal **contact potential** difference between pieces of the same metal in air and in vacuo; and M. Andauer obtained $-0{\cdot}32$ volt for the potential of nickel in air. S. J. French and L. Kahlenberg studied the gas-metal electrode of nickel in hydrogen, oxygen, and nitrogen. R. D. Kleeman and co-workers studied the negative charge assumed by nickel in contact with a liquid. The contact potential of nickel was studied by M. Forro and E. Patai, P. H. Dowling, H. Kösters, and O. Stierstadt. G. N. Glasoe found 0·20 volt for the contact potential of nickel and iron; G. Mönch measured the effect with nickel and copper, and nickel and silver; and J. E. Schrader found the contact potential of nickel and copper to be 0·25 volt, and with simultaneous heat treatment of the metal, the difference of potential was $-0{\cdot}15$ volt with high frequency, induced current. O. Scarpa, and E. Dubois also studied the **Volta effect**; and L. Bernoulli, V. Freedericksz, and A. Hesehus, the position of nickel in Volta's contact series. C. Drucker placed nickel in the **electrochemical series** . . . Zn, Fe, Cd, Tl, Co, Ni, Pb, . . . ; and B. Neumann, . . . Zn, Cd, Fe, Co, Ni, Pb, . . . G. Tammann's observations were discussed in connection with cobalt. M. Faraday, and J. C. Poggendorff observed the place of nickel in the electrochemical series in dil. sulphuric acid; S. Marianini, in sea-water with $\frac{1}{100}$th part of sulphuric acid; M. Faraday, and A. Avegadro and V. Michelotti, in dil. nitric acid; M. Faraday, in conc. nitric acid; M. Faraday, in hydrochloric acid; J. C. Poggendorff, in a soln. of potassium cyanide, and of potassium ferrocyanide; M. Faraday, in potassium hydroxide, and potassium sulphide. M. M. Haring and E. G. van der Bosche found cobalt to be more electropositive than nickel. The subject was studied by A. S. Russell and co-workers, H. T. S. Britton, E. Dubois, G. N. Glasoe, R. Vieweg, and by C. B. Gates; and J. E. Schrader examined the effect of heat treatment on the contact difference of potential. W. J. Müller and K. Konopicky showed that nickel exhibits a **motoelectric effect,** in that a current is produced in a short-circuited cell, consisting of two similar electrodes, with one electrolyte, by a movement of one electrode. T. Mashimo observed that with electrodes in a

M-soln. of ferric chloride, with agitation at one electrode, the potential at the disturbed electrode was positive, and at the undisturbed electrode, negative. S. Procopiu found the e.m.f. of nickel electrodes moving in water, in $0{\cdot}2N$-H_2SO_4, and $0{\cdot}2N$-HNO_3, to be, respectively, 0·010, 0·072, and 0·054 volt. C. E. Mendenhall and L. R. Ingersoll found that globules of metal on a Nernst's glower move against the current.

O. Erbacher [22] studied the ionic exchange with nickel and a soln. of a nickel salt; and H. Brintzinger and co-workers, the hydration of complex ions. A. Heydweiller found the **ionic mobility** of nickel, $\frac{1}{2}Ni^{\cdot\cdot}$, to be 44·2 at 18°. A. Feiler gave 50·5; K. Murata, 45·1 at 18°, and 53·0 at 25°; E. Rona, 48·0 at 18°; W. Althammer, 50·1 for the chloride, 51·1 for the bromide, and iodide; and W. Riedel gave for soln. with a mol of the salt per 21·5 and 300, the respective values 0·3616 and 0·3960. W. Ostwald calculated the **heat of ionization,** $Co \rightarrow Co^{\cdot\cdot}$, to be 68 kilojoules on the assumption that the heat of ionization, $H_2 = 2H^{\cdot}$, is zero. J. D. Bernal and R. H. Fowler calculated for the ionization energy of the $Co^{\cdot\cdot}$-ions, 580 Cals. per gram-ion.

H. von Euler [23] gave for the **electrode potential** of nickel against the calomel electrode and N-$NiSO_4$, 0·466 volt, and with $0{\cdot}2N$-$NiSO_4$, 0·472 volt; taking the calomel electrode as 0·560 volt, these data become, respectively, —0·094 and —0·088 volt. B. Neumann gave —0·022 volt for the electrode potential of nickel against N-$NiSO_4$, —0·020 volt against N-$NiCl_2$, and —0·060 volt against N-$Ni(NO_3)_2$. There is, indeed, a striking difference in the values reported by different observers for the electrode potential of nickel in a normal soln. of the sulphate. In addition to the values just quoted, N. T. M. Wilsmore and W. Ostwald gave —0·049 volt; W. Pfannhausen, —0·041 and —0·060 volt for nickel in N-$NiSO_4$ and N-$(NH_4)_2Ni(SO_4)_2$, respectively; O. Bauer, for nickel in a 1 per cent. soln. of sodium chloride, and a normal calomel electrode, —0·213 volt at the start, and —0·080 volt after 120 hrs.; A. Siemens, —0·036 volt; E. Newbery, —0·031 volt; and A. Schweitzer, —0·033 volt; N. M. Haring and E. G. van der Bosche, —0·231 volt at 25°; F. W. Küster, —0·243 volt; W. Muthmann and F. Fraunberger, —0·323 volt; and T. Heymann and K. Jellinek, —0·268 volt at 25°. Observations were also made by S. Bodforss, K. Murata, O. Erbacher, V. Sihvonen and O. Enwald, B. B. Banerji, and K. Georgi. N. R. Dhar studied the e.m.f. of soln. of potassium chloride against nickel; C. Bedel, a soln. of sodium hydroxide, hydrofluoric acid, and sulphuric acid; E. Müller and J. Janitzky used a soln. of nickel chloride; H. N. Huntzicker and L. Kahlenberg, soln. of salts of copper, silver, and nickel; and G. B. Kistiakowsky, in hydrogen, and nitrogen. S. Makishima studied the subject. E. Newbery attributed the discrepancies to the use of electrolytic nickel, or of nickel treated electrolytically before use, for he considered that under these conditions the metal contained x per cent. of occluded hydrogen or nickel hydride. He observed that the electrode potential of nickel depends largely on the method of preparing the electrode and on its subjection to intermittent anodic action. A very slight motion of the nickel electrode suffices to raise the potential 0·07 volt, and a rapid shaking of the electrode in the soln. raised the potential 0·11 volt. A current of 10^{-5} amp. is sufficient to alter the cathode potential 0·1 volt; whilst the value for the anode potential remains nearly constant until the current passing is nearly a thousand times this value. Hence, in agreement with L. Colombier, it was inferred that adsorbed hydrogen (or oxygen) affects seriously the cathode potential of nickel, although K. Murata said that hydrogen has no effect on the true electrode potential of nickel except in the presence of oxygen, which should be excluded when measurements are made. K. Georgi, and P. H. Dowling studied the subject. A. Schweitzer observed that the electrode potential of a cathode, in which nickel is being deposited, becomes more and more positive as the current density increases and as the temp. falls. At 16°, with nickel powder, charged with hydrogen, the electrode potential of nickel in N-$NiSO_4$ is —0·33 volt, and in $0{\cdot}1N$-

$NiSO_4$, −0·35 volt; whilst in N-$NiCl_2$, and 0·1N-$NiCl_2$ the potentials are respectively −0·31 and −0·36 volt—the potential of the normal calomel electrode is 0·283 volt. With sheet nickel in N-$NiSO_4$ the potential is 0·31 volt, and in 0·1N-$NiSO_4$, −0·336 volt. These results were determined in an atm. of hydrogen. The potential required to deposit nickel is higher than the values just indicated, even with the smallest current density. A. Schweitzer suggested that possibly a nickel-hydrogen alloy is formed which gives higher potentials. The potential corresponding with $Ni+2\oplus=Ni^{\cdot\cdot}$ cannot be measured if traces of oxygen are present. The potentials in an atm. of hydrogen may therefore be too high, and those without hydrogen too low. Hence, the real value for nickel in N-$NiSO_4$ lies between E. P. Schoch's value −0·2 volt, and the above mentioned −0·33 volt. A. Smits pointed out that nickel is a very inert metal, and that the presence of hydrogen ions or of molecular hydrogen can profoundly modify the electrode so that its potential becomes the same as that of a hydrogen electrode. An atm. of hydrogen should not therefore be employed for the measurements, but preferably an atm. of nitrogen, or else the containing vessel should be completely filled with the soln. which has been previously boiled in vacuo. In this way, A. Smits obtained for the potential of the nickel electrode relative to the normal calomel electrode −0·480 volt, or with reference to the hydrogen electrode, 0·194 volt. A. Oliverio and O. Belfiori studied zinc and nickel electrodes in soln. of nitrates.

E. Newbery gave −0·32 volt for the electrode potential of nickel in N-$NiSO_4$; −0·34 volt in N-$Ni(NO_3)_2$; and −0·32 volt in N-$NiCl_2$, and in N-$(NH_4)_2Ni(SO_4)_2$. He found that the electrode potential of nickel in 0·5N-$NiSO_4$ assumes three different values under different conditions, namely, −0·25 and −0·65 volt, with an intermediate value −0·53 volt at 25°. He explained this result by assuming that solid nickel contains two allotropes with normal electrode potentials approximating −0·5 and −0·0 volt respectively when referred to the normal hydrogen electrode; an equilibrium mixture of the two allotropes, at ordinary temp., has a potential of −0·17 volt. S. Triandafil studied the effect of temp. A. M. Hasebrink observed that the potential of nickel rubbed with emery in an indifferent atm. falls at first, then recovers partially, and, after repeated rubbings, the potential becomes constant at a value which is lower than the initial one.

S. J. French and L. Kahlenberg found that the potential of nickel in N-KCl in hydrogen becomes more basic, reaching a maximum and then falling, and likewise also in nitrogen; in oxygen the potential becomes less basic, reaching a maximum and then falling off in bubbling gas, but in a quiescent state the potential becomes more basic. L. Kahlenberg and J. V. Steinle observed that the single potential of nickel in 0·5N-Na_3AsO_4 is 0·216 volt; in 0·5N-K_3AsO_4, 0·241 volt; and a N-KCl sat. with arsenic trioxide, 0·228 volt. G. W. Smith and L. H. Reyerson studied the electrokinetic potential; G. Tammann and E. Jenckel, the potential in soln. of potassium hydroxide under press.; P. Bechtereff, the potential of nickel in fused sodium hydroxide; and O. Scarpa, the resistance at the contact surface of electrode and electrolyte.

M. H. Jacobi studied the cell Ni : dil. HNO_3 : soln. KCy : Zn (Cu, Cd, Sn, Ag, or Ni); J. Regnauld amalgamated and unamalgamated zinc with a soln. of zinc sulphate, nitrate, or chloride and the corresponding nickel salt and nickel; A. Schweitzer gave −0·596 volt for the e.m.f. of the cell Ni : 0·5N-$NiCl_2$: N-KCl : Hg_2Cl_2 : Hg; and C. von Neumann, the e.m.f. of the nickel-carbon cell with nitric acid, aqua regia, or sulphuric acid as exciting liquid. C. H. Prescott and M. J. Kelly studied the cell with a nickel wire anode, and an oxidized silver foil with a deposit of cæsium. N. A. Furman and G. W. Low studied the use of nickel tungsten electrodes in the electrometric titration of strong acids and bases. P. Jolibois found that a nickel salt soln. and distilled water in separate vessels connected by a U-tube, with a platinum electrode, furnished nickel hydroxide.

J. Tafel observed that the potential of a nickel cathode goes on increasing for hours, and he considered that his results do not favour the hypothesis that the

varying polarization is due to the varying thickness of a layer of gas on the electrode, but rather does the cathode surface have different catalytic effects on the process of forming hydrogen gas. E. P. Schoch gave -0.48 volt for the true equilibrium potential of nickel in N-$NiSO_4$. This value was attained in about 12 hrs. with an electrode of commercial nickel immersed in a soln. of nickel sulphate which had been boiled for some minutes, and allowed to cool in contact with air. The soln. is neutral to litmus. The potential is diminished by air or oxygen; it is increased by hydrogen, and lowered by a slight acidity of the soln. Occluded hydrogen increases the potential so that the electrodeposition of nickel does not take place until the potential is 0·2 to 0·3 volt higher than the equilibrium value, and hydrogen simultaneously appears on the electrode. The equilibrium potential of finely-divided nickel in N-$NiSO_4$ was taken to be -0.52 volt.

S. Glasstone found the cathode potential of nickel in N-$NiSO_4$, at 15°, for current densities D amp. $\times 10^{-4}$ per sq. cm., to be:

D	$0.02N$-H_2SO_4	$p_H=-2.8$	$p_H=4.0$	$p_H=5.0$	$p_H=6.0$
0·14	−0·14	−0·18	−0·21	−0·25	−0·26
0·42	−0·21	−0·29	−0·28	−0·35	−0·39
0·84	−0·30	−0·40	−0·39	−0·46	−0·50
2·80	−0·43	−0·51	−0·52	−0·58	−0·58
5·60	−0·52	−0·58	−0·59	−0·61	−0·62
12·00	−0·59	−0·61	−0·61	−0·63	−0·46
40·00	−0·61	−0·64	−0·64	−0·65	—
80·00	−0·62	−0·65	−0·65	−0·66	—

The values at 95° were:

D	$p_H=2.8$	$p_H=4$	$p_H=5$	$p_H=6$	$p_H=6$
2·8	−0·16	−0·19	−0·23	−0·28	−0·25
5·6	−0·18	−0·23	−0·25	−0·30	−0·31
12·0	−0·23	−0·28	−0·27	−0·30	−0·37
40·0	−0·29	−0·30	−0·30	−0·31	−0·44
160·0	−0·31	−0·31	−0·31	−0·31	−0·47

C. G. Fink and C. M. Decroly found that the contact potentials of nickel against sulphuric acid of the following percentage compositions are:

H_2SO_4	0·45	2·40	5·14	9·92	17·54	32·03	54·69 per cent.
Potential	−0·420	−0·598	−0·587	−0·548	−0·446	−0·471	−0·480 volt

E. Vigouroux observed that with nickel electrodes in N-Ag_2SO_4, the e.m.f. varies from -0.0021 to $+0.0168$ volt; and A. Krupkowsky gave -0.490 to -0.506 volt for the e.m.f. of nickel in N-NH_4NO_3 containing 1 per cent. each of nickel and cobalt nitrates. The potentials of nickel and of platinum in 140 c.c. of $0.1N$-soln. of nickel nitrate containing 0·4, 0·6, 0·8, and 1·0 c.c. of a 3 per cent. soln. of bromine water were measured by A. Smits. As shown in Fig. 41, the potential of the nickel anode rises immediately after the addition of bromine water, attains a maximum, and then sinks rapidly. The potential of platinum also rises at the beginning, but soon attains a state of equilibrium. Nickel is therefore greatly disturbed by the corrosive action of bromine, but this disturbance is soon compensated by the activating influence of the bromine

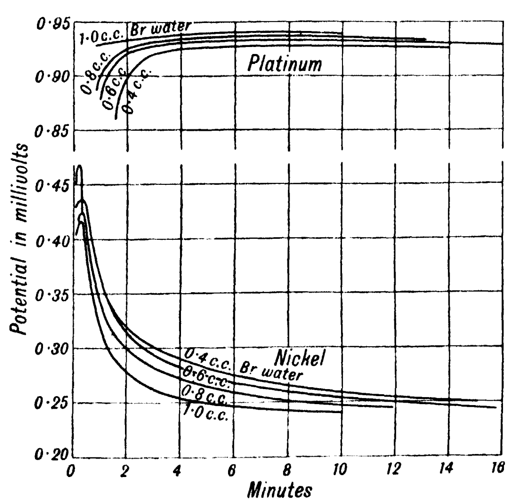


FIG. 41.—The Effect of Bromine Water on the Electrode Potential of Nickel and Platinum.

ions thus formed. The potential of nickel also falls in the presence of hypochlorite, and less so in the presence of potassium permanganate. M. Ballay examined the influence of oxidizing agents on the electrodeposition of nickel, and found that with 0·175 grm. per litre of potassium permanganate, the current efficiency was 97 per cent. without a perceptible evolution of hydrogen, but with more permanganate, the efficiency falls to 93 per cent., and the deposit is brittle. With an acidity of $p_H=6{\cdot}8$, the deposit is brittle, and the efficiency is 96·2 per cent.; with $p_H=6{\cdot}1$, the efficiency is 97·8 per cent.; and with $p_H=5{\cdot}5$ to 4·4, the efficiency is 95·4 to 94·9 per cent. and the deposit is good—*vide supra.*

According to A. Smits and C. A. L. de Bruyn, in the case of a metal like nickel which is violently disturbed by soln. containing oxygen by depositing the metal on the cathode in air, potentials can be obtained for very small current densities which are always somewhat less negative than the equilibrium potential; and this will be the case so long as the rate of cathode deposition is so small that corrosion can appreciably affect the deposited metal. For very small current densities, the potential of nickel during cathodic deposition remains less negative than the equilibrium potential; only at higher current densities does the potential become more negative, and only then does the deposition occur. The equilibrium potential is $-0{\cdot}48$ volt, and even when the current density is 200×10^{-6} amp. per sq. cm., the potential is less negative than the equilibrium potential. With a soln. of a nickel halide instead of the nitrate or sulphate, the potential of nickel passes more quickly through the value of the equilibrium potential. So long as the rate of deposition is small, the deposit can be appreciably affected by dissolved oxygen—halogen ions exert a marked catalytic influence tending to annul the disturbance. At greater current densities, the disturbing influence of dissolved oxygen will become relatively smaller, and the positive catalytic influence relatively decrease, so that if the current density is allowed to increase, the nickel potential must soon pass through the value of the equilibrium potential, and it will exhibit cathodic polarization which increases strongly at first, and afterwards more slowly.

In the electrolysis of a soln. of a metal salt, say nickel sulphate, between soluble electrodes of the same metal, nickel, the concentration of the nickel ions in the film of soln. near the cathode decreases, and increases near the anode. As a result, the cathode becomes more negative, and the anode more positive; in other words, the electrodes are polarized. The static or equilibrium potential of the metal is the single electrode potential when no current is flowing, and the dynamic potential is the single potential when the current is flowing at a specified current density; the difference between the two potentials is the **polarization** at the specified current density. If the dynamic potential is more negative than the static potential, the polarization is cathodic, and if less negative, anodic. The relations between the static and dynamic potentials of nickel in a soln. of N-$NiSO_4$, $0{\cdot}25N$-NH_4Cl, and $0{\cdot}25N$-H_3BO_3 are shown in Fig. 42 due to W. Blum, and the general treatment here is also due to him. The static potential of nickel is here assumed to be $-0{\cdot}26$ volt, *i.e.*, 0·03 volt more negative than the normal potential of nickel $-0{\cdot}23$ volt. The conc. of the $Ni^{\cdot\cdot}$-ion in this soln. is about $0{\cdot}1N$. The curve for a typical cathode current density-potential curve for nickel deposition is shown along with a typical current density-potential curve for anode polarization with active nickel. The anodic or cathodic polarization at any specified current density is equal to the difference between the potentials of the points corresponding with the equilibrium potential and the current density on appropriate curves.

The main factors tending to counteract the changes in concentration about the electrodes, and to decrease the polarization are ionization, migration, diffusion, and convection currents whether produced by changes of temp. or sp. gr. resulting from electrolysis, by stirring due to the escape of gases or external agitation. The polarization may be due not only to a change in metal-ion concentration of the adjacent soln., but also to a change in the soln. press. of the cathode. For pure

metals, such an effect is usually very slight. However, in alloy deposition, or when hydrogen is discharged simultaneously with a metal, the composition and solution pressure of the cathode may change during electrolysis, and thus may cause an effect upon the polarization. N. A. Isgarischeff and H. Ravikovitsch investigated the effect of neutral salts on the cathodic polarization of nickel; S. Triandafil, the effect of acidity. G. Athanasiu examined the effect of illuminating the electrodes; G. W. Smith and L. H. Reyerson, agitation of the electrolyte. W. J. Müller and K. Konopicky, and O. Scarpa and E. Denina studied the subject.

The potentials at the electrodes during electrolysis determine the anode and cathode efficiencies. In accord with Faraday's law, the total electrode efficiency is always 100 per cent. when all the products of electrolysis, or changes in valency, are considered—where, in electrodeposition, the valency of the metal ions is reduced to zero, the valency of metals in the free state, the cathode efficiency is determined by the proportion of current used in the discharge of the metal. It is sometimes erroneously assumed that the tendency for the discharge of hydrogen from any metal salt soln. will depend on the relative positions of hydrogen and metal in the electrochemical series; actually, the respective concentrations of $H^{\cdot}$-ions and metal-ions in a given soln. are not likely to be normal, or even equivalent to one another. In nickel-plating, the $NiSO_4$-content of the electrolyte may be about $0{\cdot}1N$, but the $H^{\cdot}$-ion content will usually be less, *e.g.*, $10^{-6}N$, or $p_H=6$. As a first approximation it can be assumed that the initial tendencies for the discharge of hydrogen and metal ions will depend on their respective static potentials in that soln. The actual proportions of metal and hydrogen discharged at any current density will be in accord with the respective current density-potential curves for metal deposition and for hydrogen discharge on that metal in that soln. W. Blum's curve for hydrogen evolution on nickel in the electrolysis of the given soln., and the curve for actual nickel deposition, are shown in Fig. 42. At any given current density the ordinate of A is equal to the sum of the ordinates of C and D. The metal cathode efficiency at that current density is equal to the ratio of the corresponding ordinates of D and A. Under these conditions, the nickel cathode efficiency will increase as the current density is increased, but can never reach 100 per cent. If, however, as in acid copper soln., the static potential of the metal is much more positive than that of hydrogen in that soln., the cathode efficiency at low current densities will be 100 per cent.. and will decrease as the current density is increased.

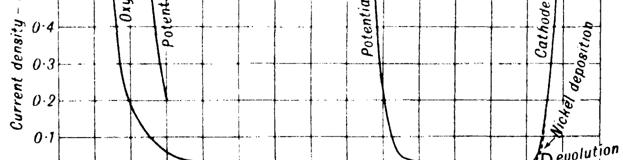


FIG. 42.—Typical Electrode Potentials during Nickel Deposition.

V. O. Krenig and V. N. Uspenskaya observed that when a base metal, immersed in acid, is coupled with a nobler metal—*e.g.* aluminium and nickel—there is a difference in the amount of hydrogen evolved against the results when the metals are not coupled. Observations were also made in cells with three electrodes—*e.g.* Al-Ni-Pt.

The shape of the polarization curves for hydrogen discharge involves the subject of **over-voltage.** In order to discharge gaseous hydrogen upon any metal surface,

it is necessary to make the potential of the latter at least as negative as that of a reversible hydrogen electrode, *i.e.*, the equilibrium potential of gaseous hydrogen in that soln. It is equally true, however, that if the metal of the cathode, *e.g.*, zinc, has a higher soln. press. than hydrogen in that soln., it is also necessary to counteract the tendency of the metal to dissolve, and to replace hydrogen. This requires the application of a potential at least as negative as that of the metal (in this case of zinc). Ordinarily the hydrogen over-voltage is defined as the excess potential beyond that of a reversible hydrogen electrode required to discharge gaseous hydrogen from that soln. either at some minimum current density or at some specified current density. If the latter definition is used, the hydrogen over-voltage is the same as hydrogen polarization as above defined. For metals more noble than hydrogen, such as copper, silver, and gold, this over-voltage is probably due principally to the concentration and state of the hydrogen in or on the metal. For metals such as tin, lead, nickel, and zinc, however, the so-called hydrogen over-voltage is largely a function of the potential of the metal itself. The potential required to deposit hydrogen with a given current density upon any cathode is a function not only of the metal (as usually emphasized), but also of the hydrogen-ion conc. of the soln., or of the cathode film. Hence the cathode efficiency as well as the character of the deposited metal may depend directly upon the $H^{\cdot}$-ion conc. of the soln. In nickel deposition the p_H of the soln. probably has a greater effect than that of any other factor. Similarly the metal anode efficiency is determined by the respective polarization curves for metal soln. and for oxygen evolution, which latter is influenced by oxygen over-voltage. With metals such as nickel, anode polarization is affected by passivity, *i.e.*, the tendency of the metal to assume an abnormally positive potential. In Fig. 42, curve F represents oxygen evolution upon nickel from a nickel sulphate soln. If the nickel becomes passive, as represented by the curve E, the anode efficiency will be lowered by the simultaneous evolution of oxygen. W. A. Caspari gave for the over-voltage of hydrogen on nickel 0·21 ; J. Tafel, 0·07 ; E. Müller, 0·03 ; A. Coehn and K. Dannenberg, 0·14 ; W. D. Harkins, 0·15 ; E. Newbery, 0·19 ; and A. Thiel and W. Hammerschmidt, 0·14. H. M. Cassel and E. Krumbein, N. Thon, H. Ficke, O. Essin, and F. Meunier studied this subject.

E. Newbery found the cathodic over-voltages of nickel, referred to the hydrogen electrode, in normal soln. of the salts, to be with current densities D milliampères per sq. cm. :

D	2	6	10	20	50	100	200	400
$NiSO_4$	0·58	0·63	0·65	0·76	0·79	0·80	0·80	0·80
$(NH_4)_2Ni(SO_4)_2$	0·45	0·68	0·72	0·74	0·77	0·78	0·77	0·75
$Ni(NO_3)_2$	0·40	0·44	0·47	0·52	0·70	0·91	0·94	0·88
$NiCl_2$	0·71	0·74	0·75	0·77	0·81	0·87	0·95	0·96
H_2SO_4	0·29	0·31	0·30	0·29	0·26	0·24	0·21	0·18
NaOH	0·18	0·20	0·20	0·20	0·21	0·21	0·21	0·22

Reduction occurs in soln. of the nitrate. Hydrogen is liberated at quite moderate current densities. The anodic over-voltages were :

D	2	6	10	20	50	100	400	1200
NaOH	0·45	0·49	0·51	0·53	0·54	0·55	0·55	0·57
H_2SO_4	—	—	—	—	—	0·62	0·67	0·68
$NiSO_4$	0·04	0·09	0·13	0·16	0·22	1·65*	1·68*	1·69*
$Ni(NO_3)_2$	0·12	0·15	1·60*	1·64*	1·67*	1·68*	1·69*	1·71*
$NiCl_2$	0·07	0·09	0·09	0·08	0·08	0·08	0·09	0·10

The asterisk indicates that the metal became passive. The anodic over-voltage of nickel is low and fairly constant, and it has similar values in acidic and in alkaline soln. It shows a slight tendency to increase with time. Nickel is a useful metal to replace platinum in cases where a low cathodic over-voltage is required, but it is very difficult to keep the over-voltage down. Roughening the surface mechanically or depositing a thin coating of rough silver on the metal depresses the over-voltage

for a time. With a current density of 10 milliampères per sq. cm. the over-voltage in acid rose from 0·18 to 0·38 volt in ten minutes, and then fell to 0·33 volt after a further twenty minutes. Interrupting the current for a few seconds causes a temporary fall in the over-voltage, but it rapidly rises to a still higher value on renewing the current. In alkali the over-voltage is much more constant, the time effect being almost nil at all current densities, although a small rise is produced by subjecting the metal to the action of a very high current density. The subject was studied by W. D. Harkins and H. S. Adams, M. Knobel, E. Denina and G. Ferrero, T. Onoda, A. Gunther-Schulze, F. Meunier, N. Kobozeff and N. I. Nekrasoff, E. Liebrich and W. Wiederholt, A. Thiel and W. Hammerschmidt, G. Jones and S. M. Christian, and T. Onoda. According to S. Glasstone, the electrodeposition potential and the over-voltage of nickel in N-soln. were respectively —0·57 and 0·33 volt at 15°; —0·43 and 0·19 volt at 55°; and —0·29 and 0·05 volt at 95°. I. Slendyk and P. Herasymenko studied the separation of hydrogen at the nickel cathode; C. Marie and G. Lejeune, the influence of colloids on the over-voltage; G. R. Hood and F. C. Krauskopf, the over-voltage of nickel cathode in connection with the electrolytic reduction of potassium chlorate; and T. Erdey-Gruz and M. Volmer, the effect of occluded hydrogen.

E. Newbery measured the cathodic over-voltage of nickel in N-$NiSO_4$ in the presence of the indicated percentages of gelatin, gum arabic, and dextrin, and found:

Current density	Nil	Gelatin 0·1	Gelatin 1·0	Gum arabic 0·1	Gum arabic 1·0	Dextrin 0·1	Dextrin 1·0 per cent.
2	0·77	0·82	0·88	0·82	0·83	0·84	0·80 volt
6	0·81	0·87	0·91	0·87	0·87	0·87	0·83 ,,
10	0·83	0·87	0·92	0·88	0·88	0·88	0·84 ,,
50	0·82	0·86	0·90	0·87	0·87	0·86	0·84 ,,
100	0·82	0·86	0·89	0·86	0·87	0·85	0·83 ,,
200	0·81	0·85	0·88	0·86	0·86	0·84	0·83 ,,
400	0·81	0·84	—	0·85	0·86	0·84	0·83 ,,
Increase	—	0·04	0·09	0·05	0·05	0·04	0·02 ,,

The over-voltage of nickel in soln. of ammonium nickel sulphate is raised 0·11 volt by the presence of 1·0 per cent. of gum arabic, whilst 0·02 per cent. of gelatin raises the over-voltage by 0·5 volt at low current densities, but depresses it by 0·01 volt at high current densities.

J. N. Pring and J. R. Curzon observed that the over-voltage increases with rise of temp. and is higher with cast and rolled sheet metal than with the electrolytic metal. The over-voltage of nickel was studied by J. W. Richards, A. Thick and E. Bruening, S. Koidzumi, F. P. Bowden and E. K. Rideal, and N. Kobozeff and N. I. Nekrasoff. According to W. J. Müller, active nickel anodes require an over-voltage of 0·4 volt to pass into soln. G. Patoux observed the relation between the current density and polarization of nickel in soln. of nickel sulphate to be:

Current density	0·9	1·3	2·3	3·0	4·4	6·7	7·1	8·6
Polarization	2·27	2·33	2·36	2·38	2·39	2·39	2·39	2·39 volts

Experiments with very conc. and very dil. soln. of the sulphate show that the conc. of the soln. has little influence on the result. A soln. containing a gram of ammonium chloride in 50 c.c. of a soln. of 62 grms. of nickel sulphate per litre, and with a gram of citric or boric acid each in place of ammonium chloride, gave:

	NH_4Cl			Citric acid			Boric acid		
Current density	0·6	1·7	4·6	0·8	3·1	6·3	1·2	2·0	3·37
Polarization	0·58	0·61	0·66	1·66	1·66	1·69	1·80	1·83	1·83 volts

D. Reichenstein attributed polarization to a slow reaction in or at passive as well as reversible electrodes due in part to the formation of compounds with the gases set free at the electrodes. U. C. Tainton found that a high current density increases the hydrogen over-voltage at the cathode. R. L. Dorrance and

W. C. Gardiner found that the anodic polarization is considerably reduced in the presence of chlorides or bromides. According to F. Förster and F. Krüger, in the electrodeposition of nickel, the addition of chlorides hinders the passage of the nickel anodes into the passive state—*vide supra*, the electrodeposition of nickel. The transitory passivity of nickel anodes is recognized by the irregularity of the potential difference, the current strength, the acidity, the current-yield, the formation of anode slime, and, in some cases, by the formation of a thick layer of nickel peroxide. C. Russo observed that chromous sulphate hinders but does not prevent the passivation of nickel anodes. The subject was discussed by F. Förster and F. Krüger, G. Grube and H. Metzger, A. Coehn and M. Glaser, E. Vogel, W. G. Ellis, H. E. Haring, A. D. Garrison and J. F. Lilley, and K. Murata. M. Schade observed that if the conc. of the acid is too small, some hydroxide as well as nickel separates out during the electrolysis of soln. of nickel salts. The polarization depends on the kind of nickel salt employed; it is greater in sulphate soln. than it is in chloride soln. The polarization is increased by the presence of $H^{\cdot}$-ions, and decreased by raising the temp. and conc. of the soln. A. Oberbeck discussed the polarization in soln. containing potassium sulphate, chloride, bromide, and iodide; and M. Krieg, various other salts. According to N. A. Isgarischeff and C. M. Ravikovitsch, the cathode polarization voltage obtained in the electrolytic deposition of nickel from nickel chloride soln. is affected by the addition of various chlorides in the order: $CdCl_2 < AlCl_3 < LiCl < CoCl_2 < MgCl_2 < NiCl_2 < NaCl < KCl < CaCl_2 < SrCl_2 < NH_4Cl < BaCl_2 < ZnCl_2$. The yields of nickel deposited per unit of current are as follow: in the presence of NH_4Cl, 68 per cent.; NaCl, 66 per cent.; LiCl, 64 per cent.; KCl, 60·1 per cent.; $MgCl_2$, 55·9 per cent.; $BaCl_2$, 52 per cent.; $SrCl_2$, 32·4 per cent.; $NiCl_2$, 35·4 per cent.; and $CaCl_2$, 30·8 per cent. of the theoretical. Of the above cations, only zinc and cadmium are deposited together with nickel on the cathode. The most lustrous deposits are obtained in the presence of lithium, sodium, ammonium, and magnesium, whilst the toughest deposits are given by the addition of the first three of these metals and of cadmium. Evolution of gas at the cathode occurs to any considerable extent only in the presence of alkaline-earth metals. N. A. Isgarischeff and N. Kudrjawzeff studied the effect of an alternating current in the electrolysis of soln. of zinc sulphate. J. W. Shipley and C. F. Goodeve found that in alternating current electrolysis there is a critical density, 4·6 amp. per sq. cm., which must be exceeded before gas is evolved from a soln. of sodium hydroxide. A. P. Rollet discussed the anodic reactions of nickel in acidic and alkaline soln.; and S. Veil, in the presence of gelatin.

According to B. Bruzs, when a current is passed between nickel electrodes in a soln. of a nickel salt the anode is at a higher temp. than the cathode, and the difference is directly proportional to the current density up to a certain value of the latter, at which there is a sudden increase in the temperature difference, attributed to the evolution of oxygen at the anode. If two nickel electrodes through which a small current has been passed for a few minutes are short-circuited, a chemically induced current, in the same direction as the impressed current, is observed when the polarization has been dissipated. This induced current is ascribed to disintegration of the lattice giving rise to enhanced activity of the loosened lattice atoms.

U. Sborgi examined the anodic behaviour of nickel in soln. of sodium chloride in methyl alcohol; U. Sborgi and G. Cappon, in soln. of ammonium and calcium nitrates in ethyl alcohol; U. Sborgi and P. Marchetti, in soln. of lithium chloride and silver nitrate in acetone; and E. Siegler and R. Cernatesco, in quinoline, glycerol, o-toluidine, aniline, nitroethane, propyl alcohol, and water.

J. Nicklès [24] observed that the **passivity of nickel** towards fuming nitric acid is produced by superficially oxidizing the metal by heating it in an alcohol flame. Purified nickel, said H. St. C. Deville, is passive in ordinary conc. nitric acid; and E. St. Edme found that whereas sheet nickel is passive in ordinary nitric acid, sp. gr. 1·4, iron is passive only in the fuming acid. Iron becomes passive slowly,

nickel rapidly, but if the two metals are introduced in the acid together, both become passive instantly. Electrolytic nickel deposited from an ammoniacal soln. of the chloride or sulphate becomes passive immediately. Iron loses its passivity when heated in hydrogen, but passive nickel remains passive although it yields a small quantity of ammonia, and acquires a silvery lustre. W. W. Hollis found that above 80°, nickel is no longer passive. H. N. Huntzicker and L. Kahlenberg said that nickel is normally passive, but immediately after cathodic treatment in a soln. of phosphoric acid, it will displace copper and silver from soln. of their salts, and reduce potassium permanganate, ferric chloride, and nitric acid. V. Rothmund observed that nickel becomes passive in sulphuric, perchloric, nitric, acetic, boric, phosphoric, citric, tartaric, oxalic, hydrofluosilicic, thiocyanic, and the halogen acids ; F. Eisenkolb, in oxy-acids ; and E. S. Hedges observed the periodic passivity of nickel.

According to M. le Blanc and M. G. Levi, at room temp. and with a current density of 0·5 amp. per sq. dm., nickel dissolves quantitatively in halides and cyanide soln., and sulphuric acid ; but in soln. of other salts it is passive ; above 80°, however, it generally loses its passivity. Nickel is passive in potash-lye even at 80° ; and it is partially passive in soln. of ammonium oxalate or sodium acetate. Increasing the current increases the passivity, but changes in the conc. of the soln. have no effect. According to M. G. Levi, if the passivity of a metal depends on the formation of an insoluble coating, it should be removed by the addition of the soln. of another salt, the anion of which forms with the metal a readily soluble salt. The behaviour of nickel in such mixtures of electrolytes indicates that the passivity of the metal in sodium carbonate or potassium hydroxide soln. may be due to the formation of a protective layer. This could, however, not be observed in the other soln. examined, so that here the passivity appears to be due to the smallness of the reaction velocity. A small addition of sodium chloride to a soln. causing passivity brings the velocity of ion-formation up to the value required for the quantitative dissolution of the metal. Sulphuric acid also acts in this way, but to a less extent than sodium chloride. The addition of sugar or acetone is without influence, but carbamide destroys the passivity, although it is uncertain whether its action is a direct one or whether it is due to its decomposition products. According to E. Newbery, nickel becomes passive in dil. sulphuric acid when a current density of 100 milliampères per sq. cm. is applied. If the current density is lowered to 50 milliampères, the well-known periodic passivation and activation are observed, being more easily produced with this than with any other metal. The potential falls from about 0·6 volt (referred to a standard oxygen electrode) slowly at first and then very rapidly to a value of about —0·5 volt, immediately rising again to near the highest value. The lower limit is very uncertain, as it is almost impossible to follow the rapid changes of potential with the usual over-voltage apparatus. The period of each " vibration " is usually from 6 to 10 seconds, and the nature is such as to suggest strongly an alternate formation and breakage of a continuous protective film over the surface of the electrode. In alkaline soln. pure nickel passivates at once, even at the lowest current densities. If the nickel contains a small percentage of copper, however, the passivity is only partial, and the nickel is dissolved and deposited in a black, sooty form on the cathode, leaving the copper adhering to what is left of the anode. For this reason, samples of nickel from different manufacturers may show widely differing resistance to disintegration. The anodic over-voltage of nickel is low and fairly constant, and has similar values in acidic and alkaline soln. W. Rathert observed that the abrupt change of the anodic potential which occurs when active nickel becomes passive has not the same value as that which occurs when the passive metal becomes active. F. Krüger and E. Nähring, W. Liebereich, C. T. Thomas and W. Blum, G. Russo, and K. Georgi discussed the subject. H. Dietrich examined the periodic phenomena in the electrolysis of nickel salts. A. Brochet and J. Petit found that with nickel as soluble anode with an alternating current, in a soln. of potassium cyanide, the

metal dissolves quantitatively so long as the current density does not exceed 2 amp. per sq. dm.; beyond this, the dissolution decreases, reaching a minimum of 80 per cent. of the theoretical when the current density is 8 amp. per sq. dm. The subject was studied by O. Sackur, and M. le Blanc, G. C. Schmidt, W. J. Müller and co-workers, E. Müller and F. Spitzer, C. W. Bennett and W. S. Burnham, F. Eisenkolb, A. D. Garrison and J. F. Lilly, D. Reichenstein, K. Murata, N. Isgarischeff, A. Adler, H. Eggert, E. Becker and H. Hilberg, O. Grube, W. Hittorf, A. S. Russell, E. Liebreich, T. Onoda, V. Rothmund, E. Grave, E. P. Schoch, E. Baumann, etc.—*vide* the passivity of iron. W. J. Müller and W. Machu studied the time of passivation of nickel—*vide* iron.

E. P. Schoch and C. P. Randolph studied the connection between the anode potential and the current density for N-soln. of nickel sulphate, and chloride, and potassium sulphate. For the current densities less than 4 milliampères per sq. dm., the nickel shows normal anodic behaviour, and the potentials are readily reproducible. This is not the case if higher current densities are used, and with excessive densities the potential falls continuously until the evolution of oxygen sets in. The chemical action which takes place as long as the potential for the evolution of oxygen has not been reached, is a quantitative soln. of nickel. There is neither a critical voltage nor a critical current density which marks the termination of the normal anodic behaviour and the transition to the passive condition. The potential and density values corresponding with this transition depend on the previous electrolytic treatment. When the current is discontinued, the potential at the anode begins to rise immediately, the rate of rise diminishing with increase in the extent of the preceding electrolysis and with diminution in the accompanying potential. It was concluded that nickel has a very small ionization velocity; in consequence of this, comparatively small current densities result in the liberation of oxygen. Whether the nickel in the passive condition is protected by a layer of oxygen or covered by an oxide film cannot be decided on the basis of the observed facts. Expressing the current density, D, in milliamps. per 100 sq. cm., and the potential E relative to the normal calomel electrode in volts:

	Active								Passive	
D .	0	0·04	0·2	2	4	22	24	32	24	185
E .	0·475	−0·463	−0·445	−0·39	−0·36	−0·27	−0·123	−0·05	+1·06	+1·131

C. A. L. de Bruyn found that with nickel nitrate the current density required to produce passivity is quite small owing to the catalytic influence of the nitrate ions. The greater tendency of nickel to become passive than is the case with iron is also shown by the behaviour of the metal in soln. of the nickel halides. With iron the disturbance produced by the halides is small, and with nickel large. W. Liebreich observed that there is a potential range in the feeble cathodic polarization of nickel in which the metal has a relatively great tendency to dissolve in the electrolyte and form a surface film of a basic salt. B. Strauss denied the theory that surface oxidation is the cause of the passivity of nickel or of nickel-chromium steels. S. Triandafil studied the effect of temp. on the polarization of nickel.

The current density required to render nickel passive is materially increased in a magnetic field. U. Sborgi and A. Borgia examined the influence of magnetism in passivity. H. G. Byers and A. F. Morgan found that the current density required to produce the passive state with a nickel anode, C without a magnetic field, and C_m with a magnetic field in nitric, sulphuric, and phosphoric acids, as well as a soln. of sodium nitrate and potassium sulphate, was:

	HNO_3			H_2SO_4		H_3PO_4		$NaNO_3$		K_2SO_4
	1 per cent.	5 per cent.	10 per cent.	5 per cent.	10 per cent.	5 per cent.	10 per cent.	N-	0·1N	0·5N
C .	247	297	892	450	471	46	39·7	3·71	2·81	2·38
C_m .	324	385	1051	550	627	51	42·1	4·46	3·13	3·00
Diff. .	77	88	159	100	156	5	2·4	0·75	0·32	0·62

C. A. L. de Bruyn found that the activation curve of nickel does not show a portion almost horizontal as in the case of iron. The oxygen taken up by nickel during anodic polarization is gradually removed by hydrogen until the nickel surface contains only hydrogen, not oxygen. The curve with nickel nitrate soln. is shown in Fig. 43. Analogous results are obtained with soln. of the nickel halides. E. S. Hedges studied the periodic passivity of nickel.

G. Grube showed that in neutral soln. the variation of the potential of the anode with current density is much more marked with nickel than with platinum, and the curves show how very strong the polarization is with the nickel anode which forms a surface film of oxide—*vide* iron.

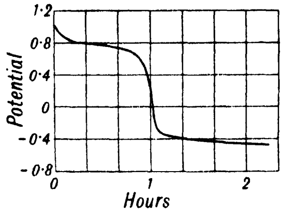


FIG. 43.—Activation Curve of Passive Nickel.

A. P. Rollet studied the electrolysis of dil. alkali-lye, or dil. sulphuric acid with nickel anodes and an alternating current, and observed that the electrode is alternately coated with oxide and powdered metal. L. Tronstad, and F. Krüger and E. Nähring observed that the X-radiograms agree with the assumption that a surface film is formed when nickel becomes passive, and, added L. Tronstad, the oxide film is not totally destroyed on activation, but it becomes porous and spongy; on re-passivation, the holes are refilled with oxide, and the film becomes thicker. W. J. Müller and co-workers studied the passivating film of oxide on nickel, and said that the greater resistance of nickel to corrosion than of iron is due to the greater stability of the oxide film. E. Müller and J. Janitzki found that rubbing the nickel makes its potential nearly reversible when in soln. of acids, bases, or neutral salts. P. K. Frolich and G. L. Clark discussed the mechanism of the deposition—*vide supra.* L. McCulloch observed cases of passivity in which a sparingly soluble film of sulphate was present. The surface film of oxide was studied by L. Tronstad, and U. R. Evans and C. Stockdale. U. R. Evans investigated the effect of passivation films on the anodic process; W. Frese, the effect of films on the photochemical effect, and passivity—*vide* the passivity of iron; and E. S. Hedges, the periodic passivity of nickel anodes. G. C. Schmidt discussed the hydrogen theory of passivity—*vide* passive iron; A. Barattini, and E. Werner, the solubility of different kinds of nickel anodes—cast, rolled, hammered, sintered, and electrolytic nickel. E. Newbery, and W. Ogawa studied the rectifying qualities of nickel and galena on the alternating electric current.

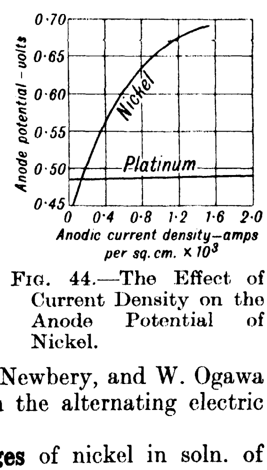


FIG. 44.—The Effect of Current Density on the Anode Potential of Nickel.

J. B. O'Sullivan[25] measured the **deposition voltages** of nickel in soln. of $NiSO_4.7H_2O$, 24 grms. per 100 c.c.; NaCl, 1·56 grms. per 100 c.c.; and $0{\cdot}2N$-NH_4- or acetate ion; and the $0{\cdot}2M$-borate ions, for current densities of 2, 5, 10, and 15 milliamps. per sq. cm. at 17° and 35°, and calculated values for unit current density. The deposition potentials were measured against a saturated calomel electrode. Some results are shown in Table III. Here the p_H voltage is the reversible hydrogen potential in the soln. against the same standard electrode. The difference between the deposition potential and the corresponding p_H voltage gives the hydrogen overvoltage. G. Sartori, R. Saxon, H. T. S. Britton, N. V. Emelianova and J. Heyrovsky, J. Heyrovsky, N. A. Isgarischeff and H. Ravikovitsch, C. Marie and N. Thon studied the subject. M. Pavlik found that nickel deposits reversibly only from soln. having concentrations of calcium or lithium chloride over $6{\cdot}4N$-soln. at room temp., or from soln. containing less of these salts at 100°. The cathode deposition potential of nickel from soln. containing large amounts of dehydrating chlorides was about 0·3 volt more positive than the potential at which nickel is

TABLE III.—DEPOSITION VOLTAGES OF NICKEL.

Buffer agent	p_H	17° Current density milliamps. per sq. cm. 1	5	10	15	p_H voltage	35° Current density milliamps. per sq. cm. 1	5	10	15
Acetate	4·4	−0·840	−0·885	−0·900	−0·915	−0·505	−0·775	−0·820	−0·845	−0·855
	5·3	−0·858	−0·915	−0·945	−0·960	−0·557	−0·784	−0·845	−0·870	−0·885
Borate	5·9	−0·833	−0·905	−0·940	−0·965	−0·592	−0·744	−0·815	−0·850	−0·870
	6·2	−0·839	−0·915	−0·945	−0·970	−0·610	−0·748	−0·815	−0·850	−0·870
	6·4	−0·847	−0·940	−0·985	—	−0·621	−0·748	−0·815	−0·850	−0·870
NH_4	5·9	−0·835	−0·930	−0·980	−1·005	−0·592	−0·762	−0·835	−0·870	−0·890
	6·3	−0·828	−0·925	−0·970	−1·000	−0·165	−0·739	−0·835	−0·875	−0·890
	6·8	−0·827	−0·920	−0·965	−0·990	−0·644	—	—	—	—
	7·0	−0·820	−0·920	−0·965	−0·990	−0·656	—	—	—	—

deposited from pure soln. of nickel chloride with the same concentration of nickel. The deposition of nickel was not affected by H˙-ions ; a slight influence of acidity was attributed to the removal of the products of hydrolysis in dil. soln. The irreversible deposition of nickel from dil. soln. is attributed to the slow dehydration of nickel ions in the inner sphere of co-ordination, whereas the reversible deposition of nickel in conc. soln. is assumed to occur from complexes [$NiCl_n$], from which the deformable chlorine ions are readily removed in the strong electric field of the cathodic surface—*vide supra*, cobalt chloride. F. Förster and K. Georgi found that the deposition of nickel does not, as supposed by S. Glasstone, commence at a definite potential which differs from the equilibrium potential, and then after proceed without retardation; for, under specified conditions, with a current density of $0·56 \times 10^{-4}$ amp. per sq. cm. no deposition occurs during the first 30 mins., but after 24 hrs. sufficient nickel is deposited to calculate the current yield. R. Müller and co-workers, and G. Devoto and A. Ratti examined the effect of organic substances. F. Braun studied some phenomena connected with the electrolysis of nickel salts. T. Kinbara observed the effect of a current with a nickel electrode on a photographic dry plate.

The **electrodeposition of nickel** has been previously discussed. V. Kohlschütter and E. Vuilleumier found that in the electrodeposition of nickel, a film is first formed on the cathode, and this is followed by a contraction of the film which causes a bending of the cathode. The contraction is dependent on the current density and the composition of the electrolyte; it is strongly influenced by the addition of other substances to the electrolyte, and is less in soln. which cause an evolution of hydrogen, and also when the deposit is fine-grained. When an already bent cathode is charged with hydrogen it straightens out again, but if the current is interrupted at this stage, the hydrogen is set free and the cathode takes up its original bent form. In soln. which do not evolve hydrogen the contraction occurs in jumps, which have the characteristics of delayed effects. The whole effect is probably due to the fact that the metal is at first deposited in a highly disperse form, and then the particles sinter with the formation of a denser material. This probably occurs along with the formation of a gas layer on the cathode, which plays the part of a dispersion medium. Since the electrolytic soln. pressure of the highly disperse form is necessarily greater than that of the denser metal, this view explains the increase in the deposition potential above that of the ordinary metal. According to H. Stäger, there are two types of contraction; in one, the contraction gradually diminishes and in the other, it gradually increases. The temp. at which the layer is formed influences the structure, and consequently the mechanical behaviour, of the deposit; since the development of a film of gas at the electrode must be rendered difficult by rise of temp., the diminished dispersivity and the resultant diminished capacity to sinter which are observed may well be due

to decrease in the deposit of hydrogen. When nickel is deposited from soln. containing depolarizers—such as hydrogen dioxide, nitrobenzene, potassium chlorate, and sodium cinnamate—the contraction of the nickel deposits is markedly diminished and their structure altered under these conditions, as should be the case if the discharged hydrogen is the ultimate cause of the effect. The subject was discussed by V. Kohlschütter and co-workers, H. Schödl, J. Prajzler, H. Marshall, O. A. Esin and A. Alfimova, R. Harr, V. P. Sacchi, and E. Bouty. For E. J. Mill's observations on the electrostriction of nickel, *vide* iron. K. M. Oesterle examined the crystal structure and physical properties of crystal deposits of nickel from N-$NiCl_2$ on platinum or silver cathodes using nickel anodes, and a cathode density of 2·5 amp. per sq. dm. The character of the deposits depends on the p_H value of the electrolyte, and also on the presence of gelatin, which, in serving as a protective colloid of the dispersed nickel hydroxide, causes a bright smooth layer to be formed. The data corresponding with those deposits obtained from soln. of p_H=4·5 to 6·0 illustrate how great an effect a small change in p_H may have on the quality of the layer. It is within this range that the electrolyte becomes contaminated with small amounts of nickel hydroxide.

E. P. Schoch and A. Hirsch, and W. D. Treadwell found that, at 18°, a soln. 0·5 normal with respect to both zinc and nickel sulphates, and 0·01 normal with respect to sulphuric acid, gave the results summarized in Fig. 45 when electrolyzed. The percentage of nickel in the zinc-nickel deposit is very low at low current densities, attains a minimum, and then slowly rises. The current efficiency at high current densities is high, showing that little current is spent in the generation of hydrogen. The results at 80° are summarized in Fig. 45. With low current

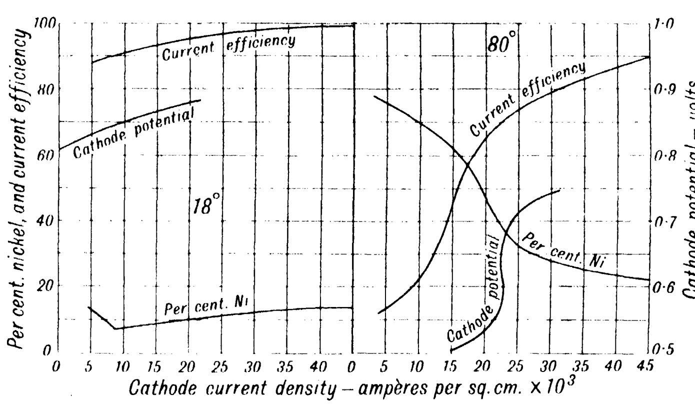


FIG. 45.—The Effect of Current Density on the Simultaneous Deposition of Zinc and Nickel.

densities, the deposit is rich in nickel, and the proportion of nickel decreases as the current density increases; at the same time, the cathode potential rises to values required for the deposition of zinc. At low current densities also, the current efficiency is below 20 per cent. and the current is spent principally in generating hydrogen. As the cathode potential rises with increasing current densities, so does the current efficiency also rise. The subject was investigated by S. Glasstone, A. Fischer, B. Bogitch, F. Förster and K. Georgi, M. Pavlik, and A. Thiel and A. Windelschmidt.

J. B. O'Sullivan found that the presence of small proportions of iron salts has no appreciable effect on the electrodeposition of nickel, owing to the preferential deposition of iron whereby this metal is removed from the cathode film before it can form colloidal compounds. On the other hand, aluminium can accumulate in

the cathode film until colloidal compounds are formed. When this has gone far enough, the character of the deposit is profoundly modified; it becomes black or "burnt." The black deposit contains appreciable amounts of aluminium, the white deposit has none. The subject was discussed by L. D. Hammond, W. C. Ellis, P. K. Frölich and G. L. Clark, K. Engemann, and G. Fuseya and K. Murata.

A. B. Schiötz found nickel alone is deposited from soln. of nickel chloride in the presence of cerous chloride. V. Engelhardt and N. Schönfeldt studied the speeds of deposition at different distances from the anode; E. Becker, the composition of the anodes; A. W. Hothersall and R. A. F. Hammond, the effect of oxidizing agents—hydrogen dioxide and nickel nitrate; and E. S. Hedges, the periodic electrodeposition. H. Forestier observed that in a magnetic field of 5200 gauss, the rate of deposition of nickel from a 0·61 per cent. aq. soln. of nickel sulphate is considerably retarded when $p_H<2{\cdot}3$, and is arrested when $p_H<1{\cdot}0$. For higher values of p_H, there is a slight acceleration. For $p_H=1{\cdot}2$, and increasing intensities of the magnetic field, the rate of deposition decreases asymptotically to a minimum.

T. A. Edison,[26] and E. W. Jungner constructed the so-called **nickel-iron accumulator** in which the charged cell had a positive electrode of nickelic oxide, and the negative electrode, finely divided iron; the electrolyte is a 20 per cent. soln. of sodium hydroxide. According to F. Förster, the reaction is:

$$\underset{\text{Discharging}\rightarrow}{Ni_2O_3.1{\cdot}2+1{\cdot}8H_2O}\rightleftharpoons\underset{\leftarrow\text{Charging}}{2Ni(OH)_2+2OH'+2\oplus}$$

The reaction during the discharge involves $Fe\rightarrow Fe^{\cdot\cdot}+2\ominus$, and $Ni^{\cdot\cdot\cdot}\rightarrow Ni^{\cdot\cdot}+\oplus$, or $Fe+2Ni(OH)_3\rightarrow Fe(OH)_2+2Ni(OH)_2$. For the energy of the reactions obtained by F. Giordani and E. Matthias, *vide infra*, nickelic oxide. The cell was studied by M. U. Schoop, A. Dinin and M. U. Schoop, Nya Ackumulator Aktiebolatge Jungner, F. Peters, A. Erb, R. Gahl, A. L. Marsh, M. Sevillano, E. Schneckenberg, A. E. Kennelly, C. F. Holmboe, F. W. Mann, W. Dinser, A. E. Kennelly and S. E. Whiting, H. Lyon, O. Schmidt, F. M. Davis, F. Sieg, H. Rodman, A. Bainville, F. Förster, F. Förster and V. Herold, G. Hagen, M. Roloff, M. Roloff and H. Wehrlin, K. Elbs, P. Krassa, O. Faust, J. Woost, O. Pattenhausen, J. Zedner, E. F. Roeber, G. Nordström, L. Gräfenberg, W. Hibbert, C. W. Bennett and H. N. Gilbert, M. de Kay Thompson and H. K. Richardson, R. Jonaust, and L. C. Turnock. W. Dinser, D. W. T. Kirkman and F. W. Mann, and F. W. Mann discussed the nickel-cadmium cell.

The **thermoelectric force** of a couple of nickel and *platinum*, for 100°, was found by J. Dewar and J. A. Fleming[27] to be −1·43 millivolts; by K. Feussner

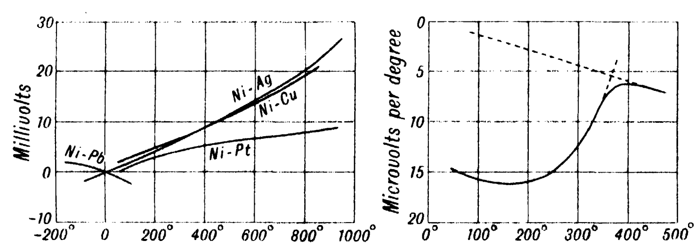


FIG. 46.—Thermoelectric Force of Nickel against Platinum, Lead, Silver, and Copper.

and St. Lindeck, −1·20 millivolts; G. Reichard, −1·94 millivolts; E. Wagner, −1·52 millivolts; K. Noll, −1·65 millivolts; W. Jäger and H. Diesselhorst, −1·62 millivolts; and P. W. Bridgman, −1·496 millivolts—*vide* Fig. 46. Nickel is thermoelectrically negative to platinum so that in a simple thermoelectric circuit of these two metals, the current flows from platinum to nickel at the cold junction.

K. E. Grew's results are plotted in Fig. 47, and they show a striking break in the curve at 360°. W. H. Ross studied the effect of longitudinally and transversely magnetized wires. Observations were made by K. E. Grew, W. Rohn, and F. E. Bash—*vide* Fig. 48. F. R. Caldwell found the e.m.f., E millivolts, of 99·94 per cent. nickel against platinum to be:

	100°	200°	300°	400°	500°	700°	900°	1100°
E .	1·485	3·105	4·590	5·450	6·165	8·105	10·695	13·625

The results are plotted in Fig. 48; there is a change in the direction of the curve in the region of the magnetic transformation. The results of W. Rohn are summarized in Fig. 48. The temp. coeff. of the thermoelectric force obtained by J. Dorfmann and R. Jaanus are indicated in Fig. 49. K. E. Grew studied the thermoelectric effect at the Curie point of nickel; and G. Tammann and G. Bandel, the effect of cold-work. L. Jordan and W. H. Swanger gave 1·485 millivolts at 100°, 6·165 millivolts at 580°, and 12·130 millivolts at 1000°. L. Holborn and co-workers gave for the thermoelectric force, E millivolts, couples of nickel and *tungsten*, and of nickel and *iron*:

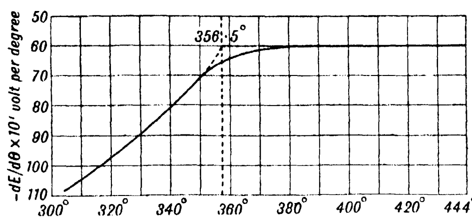


FIG. 47.—The Thermoelectric Force of the Ni–Pt Couple.

		0	100°	200°	300°	400°	600°	800°	1000°	1100°
E	W .	0·00	2·43	5·45	8·73	11·68	18·36	27·36	—	—
	Fe .	0·00	—	—	9·2	10·7	13·1	17·2	21·5	23·7

E. P. Harrison found that with the iron-nickel couple $E = -5·08$ at $-185°$; zero at 0°; 3·13 at 100°; 6·16 at 200°; 11·81 at 500°; and 15·01 at 700°. H. Broili,

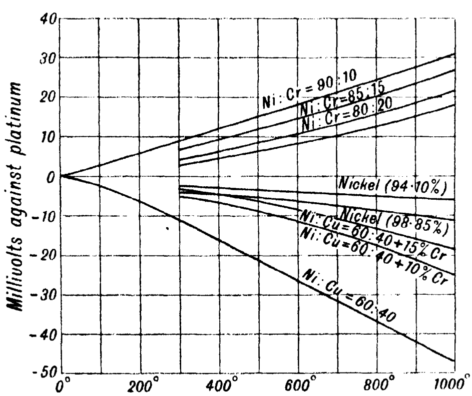


FIG. 48.—Thermoelectric Force of Nickel and its Alloys against Platinum.

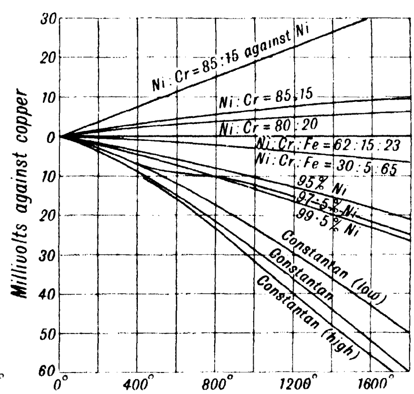


FIG. 49.—Thermoelectric Force of Nickel and its Alloys against Copper.

and W. Gerlach studied the thermomagnetic effect of *iron and nickel*. F. Hoffmann and A. Schulze found for couples of nickel against *nickel steel*, and *nichrome*:

		0°	100°	200°	400°	600°	800°	1000°	1100°
Ni-steel	60 per cent. Ni .	0·00	2·12	4·71	9·55	14·2	20·4	27·5	31·4
	35 per cent. Ni .	0·00	1·09	2·94	6·67	10·3	15·2	21·0	—
Ni-chrome	10·3 per cent. Cr .	0·00	2·20	4·71	9·67	14·6	21·0	28·3	—
	12·3 per cent. Cr .	0·00	3·52	7·47	14·9	21·8	29·4	37·2	41·2

Observations were also made by E. F. Northrup, J. Monheim, H. Lent and

F. Kofler, and M. A. Hunter and H. Jones—*vide* Fig. 50. L. Peckinger measured the effect of varying the diameter of the wires of the thermocouple. E. Rudolfi, H. Pécheux, A. W. Foster, J. J. McHenry, T. H. Pi and W. Band, and A. Krupkowsky measured the thermoelectric force of the couple of nickel and *copper*—Figs. 46 and 49. J. E. Schrader studied the effect of heat treatment; and E. Dubois found that the effect against copper becomes electronegative after the metal has been heated and cooled. W. M. Latimer, and G. von Hevesy and E. Wolff gave for a couple of nickel and *silver*—Fig. 50; R. von Dallwitz-Wegner gave $-0{\cdot}0015$ volt at 100° for the nickel and *constantan* couple; C. Dannecker, for couples of nickel and *nickel silver*, and of nickel and *cobalt*, Fig. 50; C. R. Darling and A. W. Grace, *bismuth* and nickel; and F. Hoffmann and A. Schulze, for a couple of nickel and *carbon*:

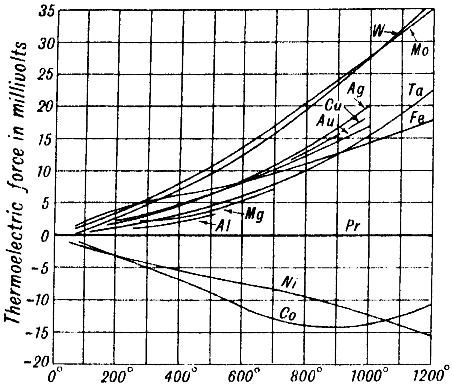


FIG. 50.—Thermoelectric Force of Nickel against other Metals.

Ni+	−185°	−80°	0°	100°	200°	400°	600°	800°	1000°	1200°
Ag	—	−1·68	0	−2·18	4·96	9·85	14·5	20·73	—	—
Ni–Ag	−0·5	−0·4	0	0·6	1·1	0·4	−2·5	−5·1	—	—
Co	—	—	0	−0·3	−1·3	−4·6	−8·7	−10·4	—	—
C	—	—	0	2·20	4·61	8·82	12·9	18·7	26·1	34·8

J. Dewar and J. A. Fleming's results for nickel against *lead* are shown in Fig. 50; and observations at low temp. were made by G. Weitzel. W. Rohn's results for nickel against *tungsten*, *molybdenum*, *tantalum*, *aluminium*, *magnesium*, *iron*, and *gold* are summarized in Fig. 50; P. W. Bridgman represented the thermoelectric force E, of nickel against lead, by $E\times10^6=17{\cdot}61\theta-0{\cdot}0178\theta^2$ volts. He also found for the thermoelectric force, $E\times10^6$ volts, of a couple of uncompressed nickel and of nickel *compressed* at a press. p kgrms. per sq. cm.:

p	10°	20°	40°	60°	80°	100°
2,000	0·12	0·25	0·54	0·87	1·25	1·68
6,000	0·41	0·85	1·82	2·88	4·02	5·24
12,000	0·91	1·99	4·00	6·32	8·81	11·44

E. Wagner gave for 300 kgrms. per sq. cm. press. between 0° and 100°, $9{\cdot}6\times10^{-12}$ volt per degree per kilogram. H. Tomlinson observed that a decrease in the thermoelectric force is produced by longitudinal traction. P. W. Bridgman obtained for the e.m.f., $E\times10^6$ volts, of a couple with unloaded nickel and of nickel in *tension* under a load of τ kgrms. per sq. cm., $E\times10^6=0{\cdot}00335\tau-0{\cdot}0_6 60\tau^2$ volts at 31°; $E\times10^6=0{\cdot}00577\tau-0{\cdot}0_5 132\tau^2$ volts at 51°; $E\times10^6=0{\cdot}0081\tau-0{\cdot}0_5 175\tau^2$ volts at 77·5°; and $E\times10^6=0{\cdot}0121\tau-0{\cdot}0_5 37\tau^2$ volts at 94·5°. M. Maclean found for a couple of nickel wires, one of which was permanently stretched longitudinally, an e.m.f. of 0·1341 microvolt per degree difference of temp. between the hot and cold junctions when the current passed from the stretched to the unstretched wire. W. del Regno observed a break in the thermoelectric power near 400°. H. Pécheux studied the effect of impurities on the thermoelectric force of nickel; H. Pélabon found that the thermoelectric power varies continuously through the m.p.; and G. Weitzel investigated the effect at a low temp. The thermoelectric properties of nickel were also studied by T. Tsutsui, and P. N. Laschtschenko and co-workers; A. Perrier and T. Kousmine, between magnetized and non-magnetized nickel; and the contact e.m.f. between solid and liquid nickel, by P. H. Dowling; the thermoelectric force between annealed and strain-hardened metal, by L. J. Newman;

the effect of ageing, by J. Thiele; the effect of cold-work, by G. Tammann; the decrease in the thermoelectric force by magnetization, by H. Tomlinson, W. H. Ross, S. R. Williams, and S. Seass.

The **Peltier effect** with nickel and copper was found by H. Jahn to be at 0°, 1·21 millicals. per coulomb; P. Cermak gave 1·90 at 0°, 2·2 at 100°, and 2·4 at 450°; E. Beck, 1·385 at 14·4°; A. E. Caswell, 1·51 at 22°; and H. C. Barker, 1·61 at 28·7°. E. Beck gave for iron and nickel, 2·288 millicals. per coulomb at 15°; for cadmium and nickel, 1·53 at 15°; and for zinc and nickel, 1·534 at 15°. A. Campbell found the neutral point with nickel and nickel silver to be 254·3°. The subject was discussed by E. H. Hall, and E. Sedström. For a couple of nickel and lead, P. W. Bridgman gave for the Peltier effect $P\times10^6=(-17\cdot61-0\cdot0356\theta)(\theta+273)$ volts; and for uncompressed nickel against nickel compressed at a press. p kgrms. per sq. cm., the Peltier effect in joules per coulomb $\times10^{16}$, is:

		0°	20°	40°	60°	80°	100°
p	2,000 . .	3·0	3·9	4·7	5·7	7·1	8·9
	6,000 . .	10·9	13·2	15·8	18·3	20·8	23·3
	12,000 . .	24·1	29·3	34·7	40·1	45·1	49·9

A. Battelli, and A. W. Foster studied the **Thomson effect.** H. E. Smith found that the Thomson effect decreases with tension by becoming less negative, until the elastic limit is reached, after which it increases. P. W. Bridgman found for the Thomson effect, σ, of nickel and lead, $\sigma\times10^6=-0\cdot0356(\theta+273)$ volts per degree; and for uncompressed nickel against nickel compressed at a press., p, the Thomson effect, $\sigma\times10^8$ joules per coulomb per degree, is:

		0°	20°	40°	60°	80°	100°
p	2,000 . .	4·4	2·1	2·21	3·8	6·0	8·6
	6,000 . .	8·6	7·4	7·2	7·2	7·3	7·5
	2,000 . .	16·4	16·5	16·2	14·6	12·2	9·6

H. E. Smith studied the effect of strain on the Thomson effect. J. Dorfman and co-workers found that the curves for the thermoelectric force of nickel against platinum show a break in the neighbourhood of the Curie point. This corresponds with a more or less rapid change in the Thomson effect—the sp. ht. of electricity. E. C. Stoner studied the problem on the assumption that ferromagnetism is due to electronic spin, and he calculated the sp. ht. per electron to be 3 cals. per gram electron—J. Dorfman and co-workers found 2·88 cals.

E. H. Hall[28] found for the **Hall effect**—*vide* iron—with nickel with a field of 9000 gauss, $R\times10^6=-4520$ at 22°; and -5910 at 57°; J. Königsberger and G. Gottstein, -2800 at 18°; H. Zahn, $-12,500$ with $H=6290$ and -4690 with $H=10,620$ at 18°; F. Unwin, -3860 at 18°; G. Moreau, $-12,300$ for $H=1700$ and -5080 for $H=13,800$ at 37°; H. Alterthum observed -1520 at $-253°$, -2800 at $-79°$, and -4700 at 18°; and for thin layers of nickel, H. B. Peacock gave $-99,000$ at 18°. A. Riede, E. Bossa, and M. Cantone and E. Bossa studied the effect with weak magnetic fields. H. K. Onnes and K. Hof found <110 for $H=11,300$ at $-270·92°$ and $-268·75°$, and <500 for $H=1300$ at $-268·75°$. A. E. Caswell gave $770\cdot7\times10^{-13}$ at 57·2°. H. K. Onnes and B. Beckman gave at $-258·5°$ for $H=4940$, 8250, and 10,270, respectively, -506, -515, and -505; at $-252·7°$ for $H=2970$, 7260, and 10,270, respectively, -498, -486, and -468; at $-183°$ for $H=2980$, 7290, and 10,440, -983, -865, and -798, respectively; and at 17° for $H=5170$, 9065, and 10,270, respectively, -6030, -4760, and -4490. W. Frey observed:

	80°	100°	150°	210°	300°	420°	620°	750°	820°
H .	4570	4590	4690	4790	4970	5280	5310	5310	5330
$R\times10^6$.	-1680	-2090	-2680	-3050	-1350	$-94·2$	$-60·2$	$-75·5$	$-77·6$

The subject was studied by J. Obata, L. J. Newman, H. B. Peacock, and E. Bossa. The relation between the Hall effect with ferromagnetic substances and the

magnetic field was studied by A. Kundt, G. S. Nielson, E. M. Pugh, and A. W. Smith and R. W. Sears—*vide* iron. O. M. Corbino, and E. P. Adams and A. K. Chapman obtained for the **Corbino effect**—*vide* iron—for a field H=1700, −32·0, and for the Hall effect, −23·7 when referred to copper unity. The effects of different fields, observed by A. K. Chapman, for the Hall and Corbino effects, are illustrated in Fig. 51. Both effects rise to a maximum, and then decrease.

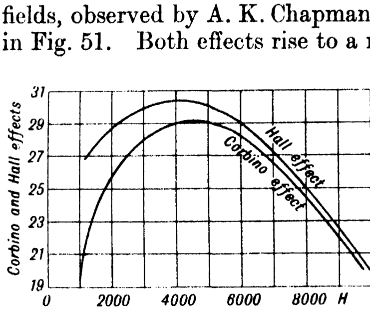


FIG. 51.—The Hall and Corbino Effects for Nickel.

E. H. Hall observed for the **Ettingshausen effect** with nickel, in a field of 9000 gauss, $P\times10^9$=60·6 at 22°, 105·7 at 57°, and 154·2 at 86°. A. E. Caswell gave $3{\cdot}67\times10^{-8}$ at 55·8°. H. Zahn gave at 18°, 176 and 28 respectively for H=6290 and 10,620 gauss; and F. Unwin, 40 at 18°. E. H. Hall observed for the **Nernst effect** with nickel in a field of 9000 gauss, $O\times10^6$=2590 at 38°, 3040 at 57°, and 3660 at 77°. A. E. Caswell gave $8{\cdot}36\times10^{-12}$ at −11·4°, and $27{\cdot}47\times10^{-12}$ at 37·6°. H. Zahn gave at 18°, 3550 and 1300, respectively, for H=6290 and 10,620; F. Unwin, 1000 at 18°; and G. Moreau, 3250 and 3800 at 37°, respectively, for H=1700 and 13,800. E. H. Hall gave for the **Leduc effect** with nickel in a field of 9000 gauss, $S\times10^9$=−528 at 38°, −494 at 57°, and −447 at 77°; A. E. Caswell gave zero at −11·8°, and $-10{\cdot}17\times10^{-7}$ at 39·4°. H. Zahn gave at 18°, −550 and −200 respectively for H=6290 and 10,620; F. Unwin gave −250 at 18°; and A. W. Smith −615 at 61° for H=10,880.

S. T'ao and W. Bond observed an e.m.f. when a magnetic field is applied parallel to a temp. gradient. P. W. Bridgman discussed the relations between these thermomagnetic effects. I. Stransky [29] studied nickel as a **radio-detector.**

K. Meyer and A. Gunther-Schulze [30] studied the cathodic spluttering of nickel. The nature of the **electric discharge** with nickel electrodes was discussed by S. R. Milner, W. B. Nottingham, A. J. Dempster, and H. Dziewulsky; the effect of the pressure of air on the sparking potential, by S. S. Cerwin; the potential difference of the arc between nickel electrodes, by C. E. Guye and L. Zebrikoff, and S. P. McCallum and L. Klatzow; the luminous discharge from nickel electrodes, by A. Voesman, J. L. Meyer, and W. C. Moore; the intensity of the ultra-violet light from the nickel arc-light, by M. Haitinger; and the cathodic spluttering of nickel, by H. P. Waran, L. R. Ingersoll and L. O. Sordahl, E. Blechschmidt, and C. H. Thomes and O. S. Duffendack—*vide supra*, nickel mirrors.

According to R. Tupputi,[31] and L. Thompson, nickel is attracted by the magnet, and its **magnetic power** is rather less than that of iron. W. A. Lampadius said that its magnetic power is to that of iron as 1 : 1·6, and W. H. Wollaston as 1 : 3 or 1 : 4. B. G. Sage, and M. Faraday studied the subject. J. Plücker said that the ratio is 4650 : 10,000; it is usually taken to be about two-thirds that of iron. C. D. Turte added that the magnetic power is destroyed by repeated heating, but this is not correct, although the metal does become non-magnetic over about 350°, but the change is reversible; and, according to J. Hopkinson, an alloy with 75 per cent. of iron is non-magnetic at ordinary temp. This illustrates the fact that two magnetic metals become non-magnetic when alloyed; but the alloy does become strongly magnetic when cooled to a low temp. W. G. Hankel observed that with small magnetic fields, the magnetism of nickel is nearly as great as that of iron, but with more intense magnetic fields, the difference between the magnetization of the metals is more marked. According to H. Becquerel, the relation between the temporary magnetization of wrought, carbonaceous nickel and that of soft iron has the following characteristics: With an increasing magnetizing force, the magnetization of nickel passes through a minimum (0·4), then through a maximum (0·75), and then attains a constant value (0·2). More or less porous cast nickel

behaves more like soft iron. Nickel is saturated with magnetism more rapidly than is the case with soft iron. The magnetization of nickel was discussed by P. Weiss, P. Weiss and A. Piccard, F. Wever, G. Falckenberg, A. Fonesca, J. Müller, K. Hayakawa, L. Néel, F. Tyler, M. Peschard, E. P. T. Tyndall and H. E. Malmström, J. Safranek, R. Reinicke, V. Retzow, T. Kahan, J. Dorfman, W. Arkadieff, D. H. Browne and J. F. Thompson, R. Sänger and co-workers, T. Spooner, N. N. Malov, A. M. Malcolm, H. Pécheux, S. J. Barnett and L. J. H. Barnett, G. Eger, and R. G. Loyarte.

C. W. Oseen gave an explanation of the non-magnetic character of many spluttered nickel films which was based on the movements of electrons. L. R. Ingersoll and J. D. Hanawalt based an explanation on the increased distance between

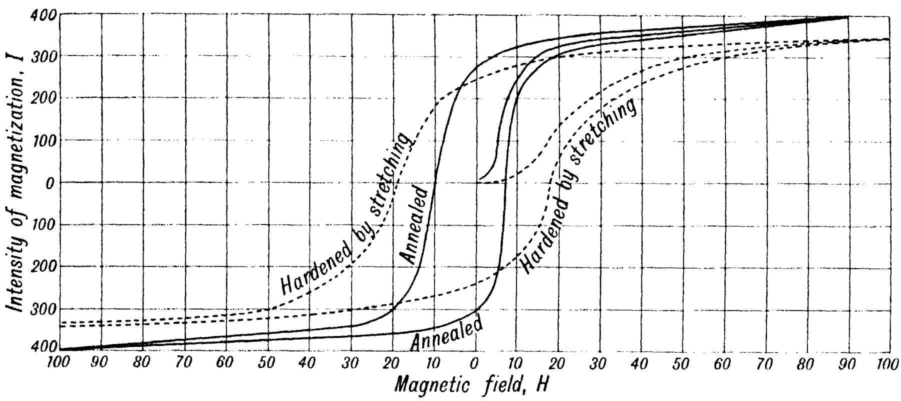


FIG. 52.—Magnetization Curves of Nickel.

the atoms when occluded hydrogen is present. The spluttered film contains much occluded gas. All agree that permeability is a very rapid, inverse function of the atomic distance. The older theories gave the inverse sixth or inverse tenth power, and later theories—*e.g.*, that of W. Heisenberg—make it an exponential function. C. Maurain studied this subject. The theory of the ferromagnetism of nickel was discussed by B. Cabrera, J. Dorfman and R. Jaanus, P. S. Epstein, A. Perrier and C. E. Borel, M. Peschard, D. Rozansky, A. Serres, J. C. Slater, E. C. Stoner, I. Tamm, F. Tyler, E. Vogt, R. H. de Waard, and P. Weiss. S. S. Bhatnagar and co-workers observed that nickel salts lose their paramagnetism and become diamagnetic when absorbed on charcoal, and this is thought to favour the view that adsorption is a case of chemical combination. The magnetism of nickel compounds was studied by D. M. Bose, B. Cabrera, O. M. Jordahl and co-workers, W. Klemm and W. Schüth, I. I. Rabi, and J. H. van Vleck.

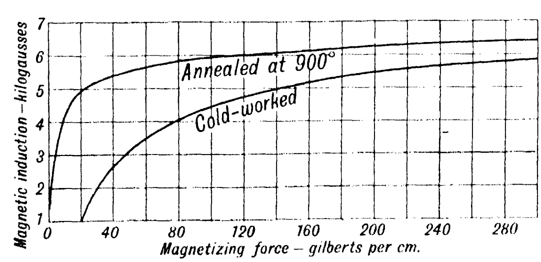


FIG. 53.—The Magnetic Induction of Nickel.

J. A. Ewing obtained for the permeability of annealed nickel the curves shown in Fig. 52. Fig. 53 shows the results with hard, unannealed nickel. The result, for the magnetic intensity, I, and susceptibility, K, for annealed nickel are :

H . .	0	4	8	10·9	24·6	52·6	79·7	100·4
I . . .	22	36	177	251	325	371	392	401
K . .	—	—	22·1	23·0	13·2	7·1	4·9	4·0

The results of the magnetic induction, B, the magnetic intensity, I, and the permeability, μ, are:

H	550	3,410	6,290	9,600	12,620
B	6,420	9,920	12,150	16,250	19,220
I	453	518	522	527	525
μ	11·67	3·12	2·57	1·69	1·52

for hard drawn nickel:

H	2,220	4,440	7,940	14,660	16,000
B	7,100	9,210	12,970	19,640	21,070
I	390	380	400	400	400
μ	3·20	2·06	1·63	1·34	1·32

and for annealed nickel:

H	3,450	6,420	11,220	12,780	13,020
B	9,850	12,860	17,200	19,310	19,800
I	510	510	480	520	540
μ	2·86	2·00	1·53	1·51	1·52

According to R. L. Sandford, the magnetic induction of 99·94 per cent. nickel varies with the magnetizing force, in gilberts per cm., as indicated in Fig. 53. The saturation value of the annealed and cold-worked metal is 6150 gausses, which agrees with the values given by A. Droz, F. Hegg, and L. W. McKeehan. P. Weiss studied the residual magnetism of nickel.

J. A. Ewing and G. C. Cowan found the following values for the relation between the intensity, I, of magnetization of annealed nickel with different magnetic fields of strength H; and similarly also with the magnetic susceptibility, χ:

H	0	4·0	8·0	10·9	24·6	79·7	100·4
I	22	36	177	251	325	392	401
χ	—	—	22·1	23·0	13·2	4·9	4·0

The results for the cyclic magnetization of annealed nickel, and of nickel hardened by stretching, are summarized in Fig. 52. The saturation value of I is one-third or one-fourth that of wrought iron. The subject was studied by W. Elenbaas, and R. Forrer and J. Martak.

C. Maurain, E. H. Williams, and S. R. Williams observed that the magnetization of the superficial layers of a rod of nickel is greater than is the case with internal layers. C. Maurain showed that, unlike iron, thin layers of nickel are more magnetic than thick layers. R. L. Edwards observed no abrupt change in the magnetic properties of nickel films of increasing thickness; and the subject was also studied by A. Aron, R. L. Edwards, W. Elenbaas, J. D. Hanawalt and L. R. Ingersoll, J. H. Howey, L. R. Ingersoll, L. R. Ingersoll and S. S. de Vinney, L. C. Jackson, H. E. Malmström, K. J. Miller, C. W. Oseen, N. H. Otis, A. J. Sorensen, and E. P. T. Tyndall and H. E. Malmström. G. Sizoo studied the effect of grain-size on the magnetization of nickel; G. Tammann, and G. Tammann and H. J. Rocha studied the effect of cold-work on the magnetization of nickel; and V. I. Gaponoff, and R. M. Bozorth, the effect of mechanical deformation. W. Kohl gave for the saturation value, $4\pi I$, of nickel with different heat treatments, with a magnetizing force, H, c.g.s. units:

	Magnetizing force	50	100	200	400	800
$4\pi I$	Annealed	1550	2680	3940	5080	5560
	4 hrs. at 400° and quenched	2200	3685	4850	5645	6040
	4 hrs. at 550° and quenched	3585	4855	5900	6300	6465
	4 hrs. at 650° and quenched	3190	4375	5615	6150	6265
	6 hrs. at 750° and quenched	4570	6070	6970	7365	7600
	6 hrs. at 950° and quenched	4375	5655	6915	7310	7590
	6 hrs. at 1250° and quenched	4885	6320	7110	7425	7425
	6 hrs. at 1000° and slowly cooled	5785	6125	6235	6295	6295

E. H. Williams studied the effect of transverse joints on the magnetization of nickel bars; H. G. Byers and A. F. Morgan, the magnetism of passive nickel and iron (*q.v.*); and S. R. Rao, S. S. Bhatnagar and co-workers, and C. G. Montgomery, the magnetic properties of colloidal nickel. C. G. Montgomery found that with a magnetic field of 3500 gauss, colloidal soln. of nickel, with benzene, water, and *iso*propyl alcohol as dispersion media, had an intensity of magnetization:

	Benzene		Water	*Iso*propyl Alcohol
Concentration Ni mgrm. per gram	0·34	0·11	0·066	0·74
Intensity magnetization, Sol	−0·00258	−0·00214	−0·00201	−0·00255
Intensity magnetization, Nickel	+0·00014	+0·00038	+0·00051	+0·00025

H. Tomlinson found that with small magnetic forces, H, the induction, B, can be represented by $B=aH+bH^2$, where a and b are constants. The internal friction in any complete cycle can be decreased by a repetition of the cycle so that the molecules appear to be accommodated by the process. The accommodation is disturbed by slight mechanical shocks, by small changes of temp., or by magnetization beyond certain limits. Under these influences, the internal friction may for a time, or even permanently, be considerably increased. For strong fields, the relation $B=H\times$constant, where the constant $4\pi I$ is nearly 6470 for nickel. P. Weiss and R. Forrer calculated by extrapolation that the saturation intensity of a gram of nickel is 3377. L. Jordan and W. H. Swanger gave 6150 gauss for the saturation value of the intrinsic induction. P. Weiss and R. Forrer observed that with most samples of nickel, a feeble magnetization proportional to the field was superposed on the regular phenomena of approach to saturation. This parasitic magnetization is zero at 0° K. The curve of J. A. Ewing and W. Low for two specimens of nickel is shown in Fig. 54. Observations were also made by T. P. Harrison, H. Gerdien, P. Plessmer, and C. A. Perkins. R. Reinicke observed for the maximum magnetic induction, B, and permeability, μ:

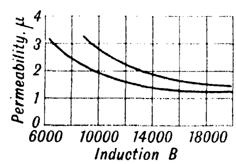


FIG. 54.—The Permeability of Strongly Magnetized Nickel.

Time		24	12	6	3	1 hrs.
$H=0·5$	B	—	—	—	28·625	25·688
	μ	—	—	—	51·04	51·30
$H=2·5$	B	—	144·38	144·28	143·15	147·98
	μ	—	58·18	57·97	57·59	59·49
$H=3·5$	B	229·75	234·00	236·45	239·83	241·90
	μ	65·78	66·85	67·55	68·44	69·10
$H=5·0$	B	492·83	504·35	509·00	515·28	523·23
	μ	98·43	100·97	101·90	103·16	104·75
$H=9·5$	B	1926	1966	1981	1978	2011
	μ	203·0	206·4	208·3	208·9	210·5

T. P. Harrison gave for the magnetic intensity and permeability of nickel annealed at 500°:

131·75°	H	3·56	7·1	10·65	17·8	26·7	35·6	44·7
	I	8·36	29·2	65·2	167·1	246·5	292·2	322·0
	μ	30·5	52·8	78·0	119·2	117·1	104·3	92·0
361·25°	H	0	8·0	9·8	13·3	22·2	26·7	44·5
	I	8·4	69·4	88·58	117·0	152·1	160·4	173·9
	μ	—	109·98	114·9	111·1	86·9	76·5	50·1
371·7°	H	5·34	8·9	13·34	22·2	31·1	40·02	44·47
	I	7·42	16·97	29·6	48·75	74·2	79·6	84·8
	μ	18·47	24·98	29·92	28·56	30·95	25·98	24·98

H. A. Rowland obtained a saturation value of 434 with a magnetizing force $H=104$. H. E. J. T. du Bois gave for moderately strong fields at 100°:

H	100	200	400	600	800	1000	1200
B	313	375	428	450	459	467	471

K. Honda :

H . .	46·2	136·5	232·5	472·5	715·5	980·5	1205·5
I . .	346	449	465	473	475	468	474

and H. Masumoto :

H . .	2·5	5·0	30·2	123·3	204	423	642
I . .	98·1	197·2	362	451	484	501	506

O. Bloch found for a field of 10,000 gauss the saturation values $B-H=4\pi I\infty$:

	−273°	−184°	25°	47°	199°	290°	309°	330°	376°
$4\pi I\infty$.	57·90	57·52	55·24	54·88	46·93	37·77	35·20	22·72	11·33

K. Honda and S. Shimizu found the intensity of magnetization, I, of nickel with different field strengths, H, at different temp. :

186°	H . .	1·42	11·35	80·4	342	704
	I . .	9	1·87	418	477	518
17°	H . .	0·53	7·92	63·8	332	703
	I . .	7	192	439	494	506
205°	H . .	1·53	5·62	207·4	334	447
	I . .	73	190	398	401	403
678°	H . .	182	343	477	—	—
	I . .	3·5	5·4	6·4	—	—
1149°	H . .	129	349	481	—	—
	I . .	2·8	5·1	5·7	—	—

S. Kaya and Y. Masiyama found that with single crystals of nickel the magnetization curves in the directions of the tetragonal, diagonal, and trigonal axes are almost straight, and coincide with each other up to an intensity of magnetization of 205. Above this intensity, the magnetization varies for the different directions of the crystal; that is, the trigonal, diagonal, and tetragonal axes are in decreasing order of magnetizability. This is the reverse of what occurs with iron crystals. The parallel and perpendicular components of magnetization in the three principal planes vary periodically with periods of 90°, 180°, and 60° when the intensity of magnetization exceeds 205°. The amplitude of these periodic variations in three principal planes is in the decreasing order of (110), (100), and (111)—*vide* iron. The (111)-axis is the direction of easiest magnetization, and this is the direction for which there is no break in the IH-curve; whilst for the (110)- and the (100)-axes, breaks occur, respectively, at $\sqrt{\frac{2}{3}}$ and $\sqrt{\frac{1}{3}}$ of the saturation. G. J. Sizoo also measured the HI-curves for single crystals. The subject was studied by W. Sucksmith and co-workers, F. C. Powell, W. L. Webster, S. Kaya and co-workers, and F. W. Constant. According to N. S. Akuloff, if a single crystal of nickel or iron is magnetized to a certain intensity, first in the direction of the principal axis, and then to the same intensity in any other direction, the difference between the resulting changes in length of the crystal parallel to the direction of magnetization, the difference between the relative changes of electrical resistance and the area between the magnetization curves, or the alteration in the internal energy are all proportional to each other—*vide* iron.

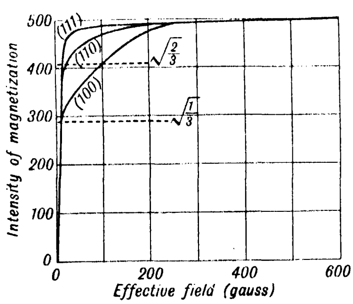


FIG. 55.—The Magnetization of Single Crystals of Nickel.

R. M. Bozorth gave for the hysteresis loop of annealed nickel the curve shown in Fig. 56 ; and J. A. Ewing, the curve shown in Fig. 57. The subject was studied by W. A. Jenkins, and W. M. Jones and J. E. Malam. R. M. Bozorth represented by Fig. 56—the curve for the corresponding Barkhausen effect, dB/dH, when $dH/dt=0{\cdot}012$ gauss per sec. The subject was studied by G. Alloco and A. Drigo,

H. Barkhausen, R. M. Bozorth and J. F. Dillinger, H. Brion, A. Drigo, W. Gerlach and P. Lertes, C. W. Heaps and co-workers, P. Kapitza, M. Kersten, H. Kühlewein, E. Maurer, L. W. McKeehan and co-workers, B. del Nuzio, L. Pfaffenberger, B. van der Pol, F. Preisach, S. Procopiu, R. E. Reinhart, J. Safranek, K. J. Sixtus and L. Tonks, K. J. Sixtus, G. J. Sizoo, C. P. Steinmetz, O. Stierstadt, M. J. O. Strutt, O. Tesche, E. P. T. Tyndall and co-workers, E. Vogt, R. G. de Waard, P. Weiss and G. Ribaud, S. R. Williams, K. Zschiesche—*vide* iron. C. W. Heaps and J. Taylor observed that with an annealed nickel wire, the Barkhausen discontinuities are small and frequent as with soft iron; and if the wire is stretched beyond the elastic limit, the effect is inappreciable, but if a single bend be put in the wire and then removed, the effect is marked. The mechanical Barkhausen effect obtained by twisting or stretching was obtained with iron and annealed nickel, but not with unannealed nickel—*vide* iron. J. R. Ashworth investigated the anhysteresis of nickel.

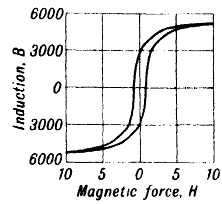


FIG. 56.—Hysteresis Loop of Annealed Nickel.

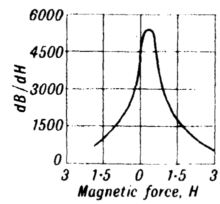


FIG. 57.—Barkhausen Data for Annealed Nickel.

H. Pécheux observed that quenching decreases the induction and increases the coercive force. The hysteresis losses of nickel were 4240 ergs when fresh, 4330 ergs when quenched, and 4750 ergs when annealed. In the equation $W=aB^{1\cdot503}$, the values of a are, respectively, 0·068, 0·073, and 0·055. A. Gaiffe found that electrolytic nickel has a large coercive force, and G. J. Sizoo observed that the coercive force of single crystals of nickel, before and after annealing, is respectively 9·5 and 2·80; and the remanence, respectively 260 and 220. G. J. Sizoo found that as the grain-size increases, the coercive force and hysteresis energy of nickel increase, the maximum permeability increases whilst the remanence remains constant. T. P. Harrison gave for the residual magnetism, the coercive force, and the hysteresis loss in ergs per c.c. per cycle for $H=45$ c.g.s. units:

	17·0°	78·5°	107·05°	164·2°	231·7°	309·75°	352°
Residual mag. .	168·5	145·0	137·5	130·0	120·0	75·0	250
Coercive force .	13·2	12·0	11·0	10·0	8·0	4·12	1·25
Hysteresis loss .	12,700	10,700	9,600	8,200	5,800	2,600	450

R. Gauss studied the coercive force of nickel; and, according to R. Gans, the coercive force of nickel ranges from 29 to 3·918 gauss as the temp. rises from that of liquid air up to 612°.

J. R. Ashworth studied the relation between the strength of an alternating current, and the intensity of magnetization. G. Potapenko and R. Sänger, W. Arkadieff, and M. J. O. Strutt studied the magnetization in fields of high frequency; H. Israel, the permeability produced by Hertzian waves; and M. Tschetverikova, the demagnetization of the metal in damped, magnetic alternating fields, and in short Hertzian waves. Demagnetization was not observed with undamped waves. B. Wedensky and M. Theodortschik observed that the permeability of nickel, with waves of wave-length between 54 and 705 metres, has a maximum at 88, 100, and 180 metres. Observations were also made by W. Arkadieff, and E. M. Guyer. H. Israel found that the apparent permeability spectrum of nickel under the influence of short Hertzian waves shows numerous maxima for waves up to 50 cm., after which the maxima are fewer, and not so pronounced. According to R. G. Loyarte, the magnetic permeability, μ, increases as the frequency, n, of the Hertzian oscillations increases, then remains constant, and does not decrease as the results of W. Arkadieff indicate:

$n\times10^6$.	0	3·75	5·4	6·33	748	300	495	952
μ . .	13	15·3	13·6	14·7	15·8	14·6	18·0	16·8

R. G. Loyarte calculated for the constants of the elementary magnet of nickel: moment of inertia, $3{\cdot}47\times10^{-38}$; natural frequency, $1{\cdot}042\times50^{11}$; logarithmic decrement, $0{\cdot}5\times10^{10}$; diameter, $0{\cdot}62\times10^{-6}$ mm.; and molecular field, 3×10^{6}. Observations were also reported by R. Gans, and R. Gans and R. G. Loyarte. O. Dahl and J. Pfaffenberger studied the magnetic anisotropy of nickel; and S. Procopiu and N. Florescu, the demagnetization of nickel.

O. Bloch found the magnetic susceptibility of nickel at

	516°	609°	665°	719°	739°	779°	840°	874°	925°
$\chi\times10^{6}$.	44·00	24·92	19·89	16·69	15·74	13·78	12·23	11·26	10·19

M. Faraday inferred that all metals might be ferromagnetic at a low enough temp. It just happens that nickel and iron have transformation temp. above atmospheric temp. The temp. of magnetic transformation, or the **Curie point,** has been previously discussed. L. H. Adams and J. W. Green found that press. had no perceptible influence on the critical point. The Curie point was also studied by L. F. Bates, R. Forrer and A. Hoffmann, H. Kühlewein, L. Néel, W. del Regno, S. Procopiu and T. Farcas, D. Rozansky, H. Tomlinson, and F. Tyler; the effect of press. on the Curie point, by D. P. Ray-Chaudhury, and the null-effect of stresses on the Curie point, by L. Tieri. L. Tieri found that the temp. is 355° for wires both unstretched and stretched by a weight of 7 kgrms. P. Weiss and G. Foëx found Curie's law holds for nickel, but at low temp., the points for the reciprocal of the susceptibility do not lie on a straight line, but rather on two straight lines, with a point of intersection at 412°. They accordingly speak of β_1- and β_2-regions. This was not confirmed by E. M. Terry, who was unable to obtain any values for the Curie constant. H. Wilde said that in general the magnetization of magnetic substances decreases with a rise of temp. for small and large magnetizing forces, and that the apparent increase with heated nickel is due to a surface resistance which disappears on raising the temp., on increasing the magnetizing force, or on diminishing the mass of the substance acted upon. The effect of temperature on the magnetic susceptibility was studied by A. Townsend, E. Englert, W. Gerlach, K. Honda and Y. Ogura, F. E. Lowance and F. W. Constant; and R. Ruer and K. Bode, E. M. Terry's observations are summarized in Fig. 58. Of the three ferromagnetic metals—iron, cobalt, and nickel—nickel alone shows a tendency to obey Curie's law—*vide* iron. If the data are plotted on a much larger scale, the reciprocal of the susceptibility curve immediately above the transformation point shows a distinct concavity upward until about 500°, after which there is an interval of about 400°, where it is straight. Between 900° and 1000° it curves downwards, and then continues straight up to the m.p. There is no change in the magnetic behaviour as the metal passes through the m.p. 1452°. The course of the curve shows that there are three distinct regions for nickel above the transformation point for β-nickel—*vide supra.* J. R. Ashworth's relation—*vide* iron—for nickel is $(H+92I)(I^{-1}-0{\cdot}00196)=20{\cdot}8T$, and the critical temp. is $T_c=388°+273°$. The results of C. S. Yeh are summarized in Fig. 58. B. del Nuzio observed no relation between the space lattice and the magnetic properties. C. Williams gave $3{\cdot}24\times10^{-4}$ for the ferromagnetic change in volume per unit volume of nickel; but, according to J. A. Hedvall and co-workers, there is no evidence of any change in the macrostructure of nickel at the Curie point. P. Chevenard used the thermomagneto-meter to detect heterogeneity in high nickel alloys.

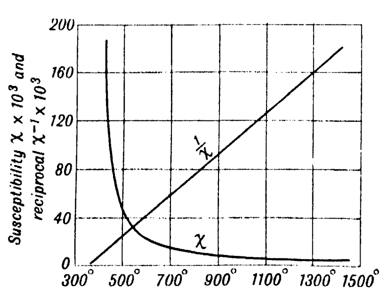


FIG. 58.—The Effect of Temperature on the Magnetic Susceptibility of Nickel.

D. Radovanovitch found that below the transformation point, the initial susceptibility and the initial slope of the $H\chi$-curves increase with temp.; from room temp. to the critical temp., the initial slope of the $H\chi$-curve increases proportionally with the 4th power of the initial susceptibility; the initial susceptibility tends to zero as the temp. tends to absolute zero; and the displacement of the temp. of the transformation point is proportional to the sq. root of the applied magnetic field. Observations were made by P. Weiss and co-workers, R. Forrer and A. Hoffmann, F. Tyler, and J. Towbridge and S. Sheldon. Y. K. Hsü and W. Band studied the thermomagnetic hysteresis of nickel.

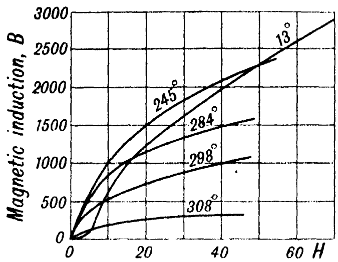


FIG. 59.—The Magnetization of Nickel at Constant Temperature.

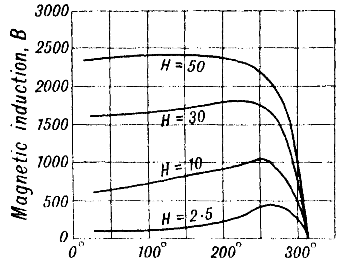


FIG. 60.—The Magnetization of Nickel with Constant Magnetic Forces.

J. Hopkinson measured the magnetization curves of a sample of 95 per cent. nickel with a critical temp. at about 310°. Just below the critical temp., the magnetic susceptibility diminished rapidly with rise of temp., but there was not so rapid a loss as that which occurs with iron under weak magnetizing forces when approaching the critical temp. At low temp., the susceptibility increases with rise of temp. when the magnetic force is low, but decreases with rise of temp. when the magnetizing force is high—Figs. 59 and 60. In Fig. 59, at 245°, there is a marked gain in susceptibility for forces between H=45 to 50. The curves show a marked loss in magnetic qualities when the temp. is sufficiently raised. The curves, Fig. 60, show the effect of temp. on the induction when the magnetizing force is constant. The effect of low temp. is greater with nickel than with iron; the critical point is lower with nickel than with iron; and the transition is less abrupt with nickel than it is with iron. The physical changes accompanying the transition are not so marked with nickel as with iron. J. Hopkinson, for instance, observed no abrupt absorption or evolution of heat by the cooling metal.

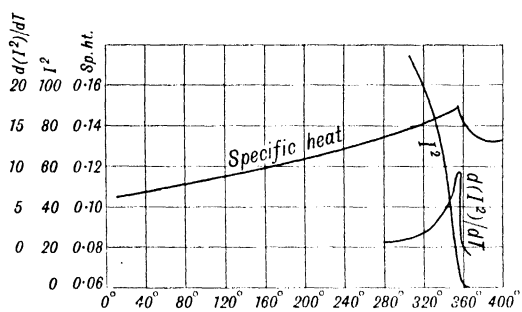


FIG. 61.—The Magnetization and Specific Heat of Nickel.

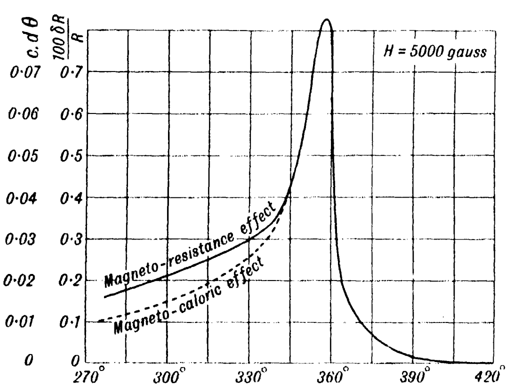


FIG. 62.—The Effect of Temperature on the Change of Resistance and the Magnetocaloric Effect.

W. Sucksmith and co-workers studied the application of P. Weiss' theory of sp. ht. and magnetization, and the results, summarized in Fig. 61, are not considered to be in agreement with theory. H. H. Potter measured the energy of magnetization in terms of the magnetocaloric effect—the product of the sp. ht., c, and the change of temp., $\delta\theta$. The change of resistance (continuous curve, Fig. 62), as indicated by W. Gerlach and K. Schneiderham, is proportional to the changes in magnetic energy (dotted line, Fig. 62). Observations were also made by P. Weiss and R. Forrer, and by A. Perrier and H. K. Onnes. A. Townsend discussed the temp. changes accompanying the magnetization of nickel; and the thermal effect of magnetization was also studied by F. Bitter.

The effect of press. and deformation on the magnetization of nickel was studied by D. P. Ray-Chaudhury, V. I. Gaponoff, and L. H. Adams and J. W. Green. E. Bauer discussed the relation between the compressibility and the magnetization of nickel. C. S. Yeh measured the effect of hydrostatic pressure on the magnetization of nickel, and found for the induction, B, the magnetizing force, H gauss, and the press. coeff. $\delta B/B_0$ per cent. per 1000 kgrms. per sq. cm., at 20°:

H	0·223	0·624	1·388	2·01	6·69	11·15	15·61	22·30
B	33	118	402	692	2000	2910	3640	4360
$\delta B/B$	2·5	4·2	5·62	4·97	3·87	2·32	1·37	0·71

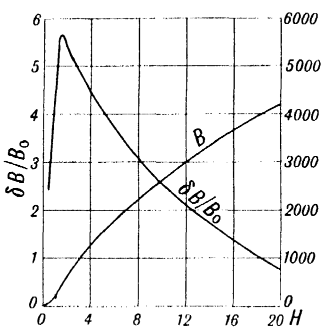


FIG. 63.—The Effect of Pressure on the Magnetization of Nickel at 20°.

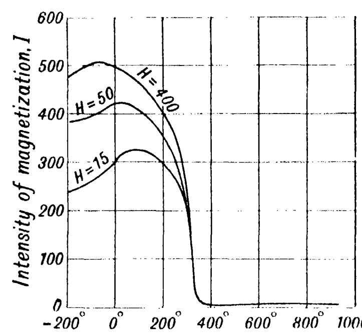


FIG. 64.—The Effect of Temperature on the Intensity of Magnetization of Nickel.

The results are plotted in Fig. 63. The temp. coeff.—per cent. per degree—and press. coeff.—per cent. per 1000 kgrms. per sq. cm.—are as follows:

H		0·223	0·624	1·338	2·01	4·46	8·92
Temp. coeff.	$p=0$	0·570	0·587	0·238	0·12	0·069	0·039
	$p=7300$	0·670	0·472	−0·053	−0·147	—	—
Press. coeff.	24·8°	2·5	4·2	5·62	4·97	—	—
	99·8°	3·1	4·6	2·02	1·53	0·6 3	0·32

Lord Kelvin noticed that pulling decreased, and relaxing the pull increased the induced magnetism of nickel in the earth's magnetic field. The effect with nickel is greater than with the other magnetic metals, but with nickel there is not the complication with the villari reversal observed with iron and cobalt. J. A. Ewing and co-workers showed that the permeability of nickel is sensitive to stress, being greatly reduced by tensile stress, and increased by compressive stress as indicated by the curves for annealed and hard (unannealed) nickel—Figs. 65 and 66; again, if nickel be magnetized while under the longitudinal stress of a constant load, the susceptibility is greatly reduced as indicated by the curves, Fig. 65, for loads corresponding respectively with 2 and 12 kgrms. per sq. mm. The effect of the tensile stress in depressing the magnetization curve is very marked. The susceptibility with no load is about 15; with a load of 2 kgrms. per sq. mm. it is about 8; and with a load of 12 kgrms. per sq. mm. the maximum susceptibility is not attained when H is raised to 100. The effect on the retentivity is even greater than it is on

the susceptibility. The dotted lines, Fig. 66, show the residual magnetism on withdrawing the magnetic force, H, at each of a series of stages, during the process of magnetizing under each load. The presence of a load reduces the residual magnetism even more than it reduces the total induced magnetism. As observed by H. Tomlinson, the amounts of magnetism which disappear when the magnetic force, H, is removed is, with a strong force, greater for a small load than it is for no load, and less again for a large load. The presence of a small load, added J. A. Ewing, may be said to increase the susceptibility of nickel with respect to that

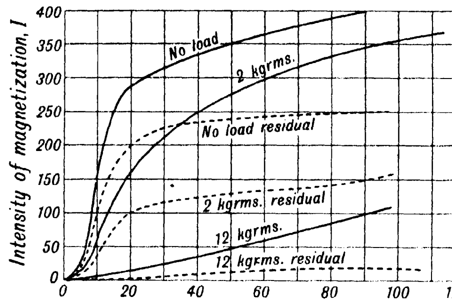


FIG. 65.—Magnetization of Annealed Nickel by Longitudinal Tensile Stress.

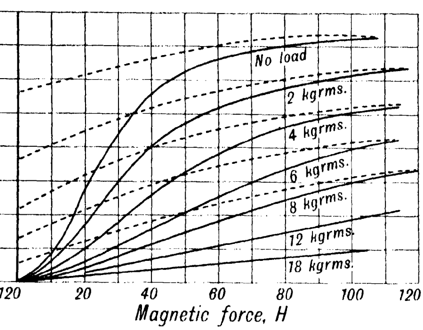


FIG. 66.—Magnetization of Nickel by Longitudinal Tensile Stress.

part of the magnetism which comes and goes when the magnetizing force, H, is alternately applied and removed, provided H is strong; when H is weak, the effect of the load is to reduce the susceptibility alone. In a similar experiment, Fig. 68, with hardened nickel, the maximum susceptibility with no load was about 8, but under a load of about 19·8 kgrms., eq. to 50 kgrms. per sq. mm., with H up to 100 c.g.s. units, the value was about half, and the residual magnetism was almost nil. The dotted lines in Fig. 66 show the effect of gradually removing the strongest value of H which has been reached in the process of magnetization. The curves

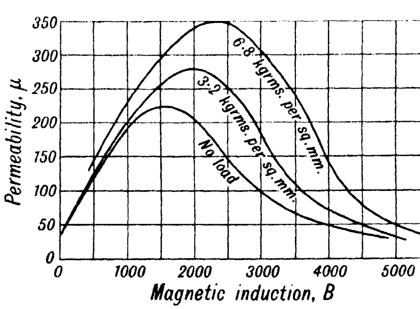


FIG. 67.—The Permeability of Feebly Magnetized Nickel—Annealed.

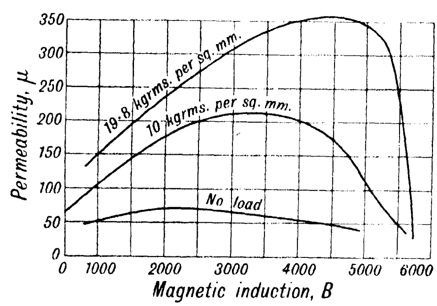


FIG. 68.—The Permeability of Feebly Magnetized Nickel—Hard.

illustrate how the residual magnetism becomes smaller when heavier loads are used. The subject was studied by J. Russell.

J. A. Ewing and co-workers showed that the susceptibility and retentivity of nickel are augmented by longitudinal compressive stresses. Fig. 69 shows the effect of compressive loads in kgrms. per sq. mm. on the induced magnetism, I; and Fig. 70, the effect of these loads on the residual magnetism observed by withdrawing the magnetic force, H, at a number of stages during the observations on the magnetization curve. The curves of the induced magnetism bend over sharply under the heaviest stresses when H is about 20. The approach towards saturation is very rapid, and the change from a state of high to one of low susceptibility is also

abrupt. In Figs. 71 and 72, the curves are plotted in a different way, so as to show the permeability, μ. A corresponding set of observations for annealed nickel are summarized in Fig. 71.

J. A. Ewing showed that magnetized nickel when subjected to cyclic variations of pull by loading and unloading with suspended weights suffers a reduction of magnetism with load, and an increase of magnetism without the load. This happens whether the magnetism be induced or residual. The results with a

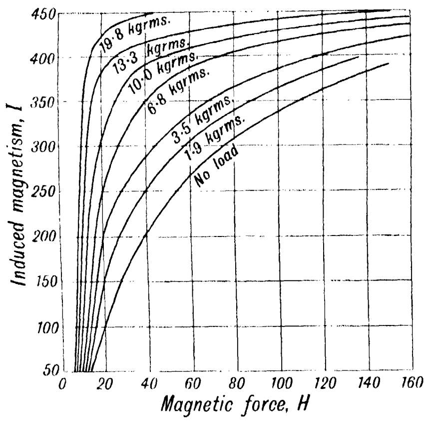


FIG. 69.—The Effect of a Compressive Load on the Individual Magnetization of Hard Nickel.

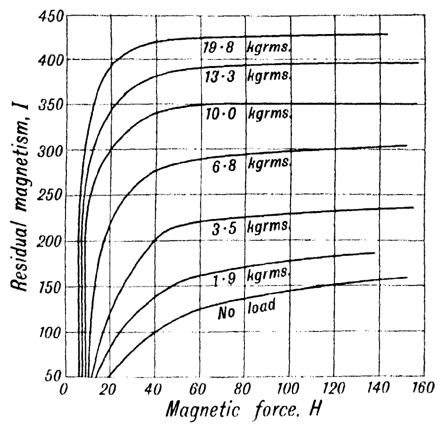


FIG. 70.—The Effect of a Compressive Load on the Residual Magnetization of Hard Nickel.

magnetizing force of 116 c.g.s. units are summarized in Fig. 72. There is some hysteresis. The curve for loading lies above that for unloading, even when the cyclic variations of stress are repeated often enough to make the magnetic changes cyclic. There is less hysteresis with hardened nickel.

Lord Kelvin showed that transient currents are produced by twisting a longitudinally magnetized nickel rod, and these currents take the opposite direction to

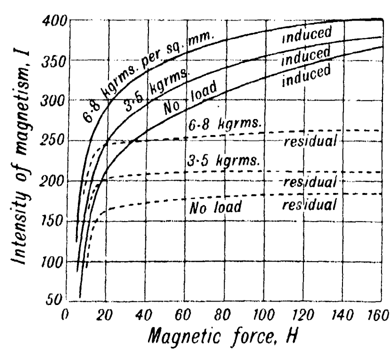


FIG. 71.—The Effects of Compressive Stress on the Induced and Residual Magnetism of Annealed Nickel.

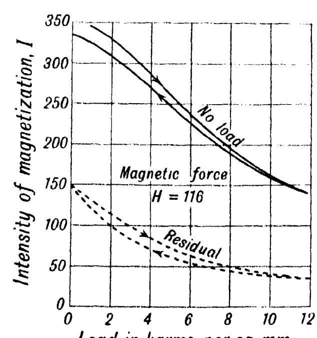


FIG. 72.—The Effect of Loading and Unloading on the Magnetism of Annealed Nickel in a Constant Field.

those produced in iron. L. Zehnder, and H. Nagaoka observed that when a nickel wire is twisted as a right-handed screw, the transient current flows from the south to the north pole. When magnetic metals are magnetized, three successive stages can be broadly detected : (i) in the early stage, the susceptibility is small, and the curve of magnetization has an easy gradient ; (ii) in the middle stage, the susceptibility is high, and the magnetization curve bends upwards and rises rapidly to a

turning-point ; and (iii) the last stage occurs when the metal has passed the turning-point, and it approaches a state of saturation. In general, the three merge one into the other. H. Nagaoka showed that with torsion, or torsion accompanied by longitudinal pull, the three stages differentiated to a far greater extent. The results shown in Fig. 73 were obtained with a magnetizing force of about 30 c.g.s. units, and with a twist of about 3° per cm., and a comparison with the dotted curve for the magnetization without torsion shows that the initial susceptibility is lowered by torsion ; the first stage of magnetization with torsion is more sharply differentiated than without torsion ; in the second stage, the twisted wire has a great differential susceptibility, and the turning-point is sharp ; and finally, by comparing the curves obtained by removing the magnetizing force, the retentivity of the twisted wire is greater than that of the other. It was also observed that when the angle of twist is greatly increased, there is a tendency to revert to the normal type for untwisted wire. The phenomenon was studied by G. Wiedemann, and H. Gerdien.

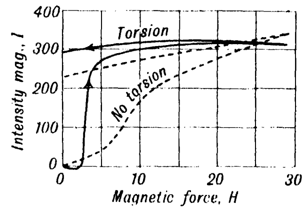


FIG. 73.—The Effect of Torsion on the Magnetism of Nickel.

H. Nagaoka examined the effect of combining torsion and longitudinal pull, Fig. 74. Pull alone lowers the magnetization curve of nickel ; when twist is superposed, the initial part of the curve is still further lowered, but with a moderate magnetizing force, the differential susceptibility suddenly rises to a large value. There is then a turning-point, and saturation is then slowly approached. H. Nagaoka also found that if the torsion be subjected to cyclic reversals, the curve connecting the magnetism with the angle of twist is nearly symmetrical, as is the case with iron, excepting that with nickel, the magnetism increases with twist instead of diminishing as in the case of iron. If the twisting to and fro be repeated whilst the nickel wire is subjected to a constant longitudinal pull, the curve is no longer symmetrical ; the magnetism is increased by twisting the wire to the side towards which the earliest twist is directed, and twisting to the other side does not increase the magnetism nearly so much. If the pull be great enough, the want of symmetry is such that whereas twisting towards one side increases the magnetism, twisting to the other side decreases the magnetism. Indeed, the decrease may be great enough to make the polarity reverse its sign. Iron does not reverse its polarity under the combined influence of pull and twist. G. Ercolini studied the behaviour of nickel in continuous and alternating magnetic fields when subjected to cycles of torsion or tension.

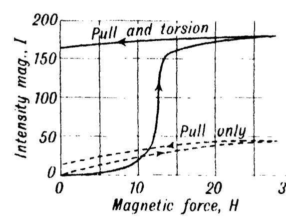


FIG. 74.—The Effect of Pull and Torsion on the Magnetism of Nickel.

When a longitudinal pull is applied to a bar of iron (*q.v.*), the magnetic induction increases with a weak magnetic field, and decreases in a strong field. The point where the effect of tension is reversed is called the Villari reversal point. There has been some discussion by A. Heydweiler, T. Gnesotto, R. Becker and M. Kersten, F. C. Powell, J. S. Rankin, A. Schulze, L. F. Miller, S. Meyer, and K. Honda and S. Shimizu as to whether or not nickel shows the Villari reversal point exhibited by iron. S. R. Williams showed that if any extraneous magnetic field is present, the Villari point may appear, but when the extraneous field is removed, the phenomenon no longer occurs. K. Honda and K. Kido found a contraction for the magnetostriction of nickel (92·3 per cent.) :

H . .	16·6	51·6	90·5	189·6	389·6	589·6
$\delta l/l \times 10^6$.	$-2·63$	$-11·07$	$-16·58$	$-21·71$	$-23·85$	$-24·60$

J. J. Thomson showed that the Joule magnetostrictive effect is the reciprocal

of the Villari effect. If a rod of metal has its magnetic induction decreased by tension, then that rod will shorten for those fields where the magnetic induction is decreased by tension; and conversely, a rod will lengthen for those magnetic fields in which tension increases the flux. The principle of H. le Chatelier applies (**2.** 18, 4). Consequently, if a metal shows the Villari effect, it will also show a reversal of sign in the change in length as the field increases from zero to higher values. If nickel shows the Villari effect, it will show the magnetostrictive effect and lengthen for weak magnetic fields and shorten for strong ones. Rods of nickel were subjected to different degrees of cold rolling so that the thin plates were progressively harder than the thicker ones. The thin strip in Fig. 75 was decreased 93 per cent. more than the thick one. The effect of a magnetic field on the change in length is shown by the two continuous curves in Fig. 75, and the dotted line in that figure shows the change in length with nickel hardened by cold work in a field of $H=58{\cdot}88$ gauss. The result shows that the shortening occurs for all field strengths up to 1200 gauss, and the tension-magnetization curves exhibit no sign of Villari reversal points. The subject was studied by H. Tomlinson, and S. R. Williams.

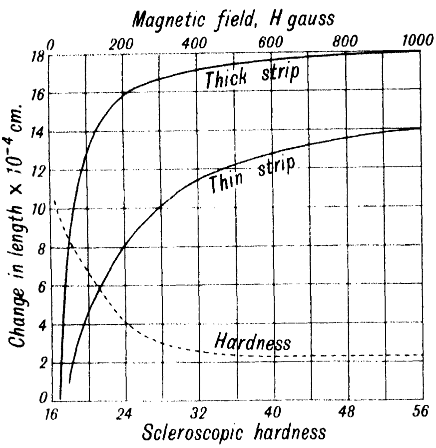


FIG. 75.—The Effect of a Magnetic Field on the Change in Length of a Nickel Rod.

W. F. Barrett found that whilst strain alters the magnetization of a metal, the effect is reversible, for magnetization is accompanied by strain. S. Bidwell found that in the case of nickel, the metal contracts when magnetized. The contraction expressed in ten-millionths of the length is illustrated by the curve, Fig. 76. The effect of tensile stress, with a moderate magnetizing force, is first to raise the curve in its earlier stages making the amount of magnetization less when the test is made while there is a pull than when there is no pull. With a stronger field, the contraction is increased by the presence of a small amount of pull, and decreased by the presence of a large amount of pull. W. Brown and P. O'Callaghan found that the rigidity of nickel increases in a direct, longitudinal field until it reaches a maximum in a field of 26 c.g.s. units, it then decreases rapidly to a minimum in a field of 41 c.g.s. units, and thereafter it increases with the field. The curve follows the same general shape with alternating fields. With transverse fields, the rigidity slightly decreases, and then steadily increases as the applied field is augmented. A. Schulze, and A. W. Smith studied the subject. W. A. Dean obtained the results indicated in Fig. 77 for the effect with nickel, starting from the demagnetized state and increasing the applied field. There is a hysteresis effect, for when the applied field is reduced to zero, it returns to its original state along another curve. K. Honda and T. Terada observed that the magnetostriction change in length $\delta l/l\times10^6$, with magnetization, is 0·02 for $H=2{\cdot}1$, and $-44{\cdot}9$ for $H=389$ with a tension load of 1540 grms. per sq. mm., and from zero with $H=3{\cdot}8$ to $-48{\cdot}4$ with $H=390$, when the load is 5240 grms. per sq. mm. The effect with commercial nickel is similar, but rather smaller.

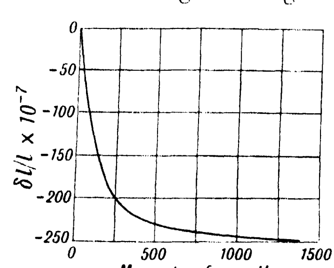


FIG. 76.—The Magnetostriction of Nickel.

A. Kussmann and B. Scharnoff observed no relation between the coercive force

and the mechanical hardness; M. Kersten, and H. Hanemann and P. D. Merica studied the relation between the magnetic properties and the elasticity of the metal. According to K. Honda and T. Terada, the change of elasticity, $\delta E/E \times 10^2$, with magnetization for pure nickel with a load of 1540 grms. per sq. mm. is $-0{\cdot}05$ for $H=4{\cdot}5$, $-14{\cdot}40$ for $H=37{\cdot}7$, and $2{\cdot}19$ for $H=406$, and for a load of 4498 grms. per sq. mm., the change is $-0{\cdot}40$ for $H=11{\cdot}6$, $-9{\cdot}90$ for $H=99{\cdot}6$, and $-0{\cdot}83$ for $H=390$. With commercial nickel, for a load of 1326 grms. per sq. mm., the change is $-0{\cdot}65$ for $H=7{\cdot}6$, $-1{\cdot}96$ for $H=52{\cdot}1$, and $1{\cdot}42$ for $H=383$; and for a load of 3874 grms. per sq. mm., the change is 0 for $H=6{\cdot}8$, $-3{\cdot}26$ for $H=76{\cdot}7$, and $0{\cdot}78$ for $H=398$. The change of the rigidity of nickel, $\delta K/K \times 10^{12}$, with magnetization is $-0{\cdot}21$ for $H=3{\cdot}9$, $-6{\cdot}80$ for $H=78{\cdot}2$, and $2{\cdot}12$ for $H=406$ with a load of 1158 grms. per sq. mm.; and $-0{\cdot}01$ for $H=11{\cdot}8$, $-8{\cdot}59$ for $H=287$, and $-6{\cdot}35$ for $H=382$ for a load of 9075 grms. per sq. mm. The change of Poissan's ratio $\delta\sigma/\sigma \times 10^{12}$ with magnetization is $-6{\cdot}1$ for $H=30$, 50 for $H=150$, and 7 for $H=250$. The change of magnetization δI_i with initial loading, and δI_c with cyclic loading for loads in tension, I grms. per sq. mm., is:

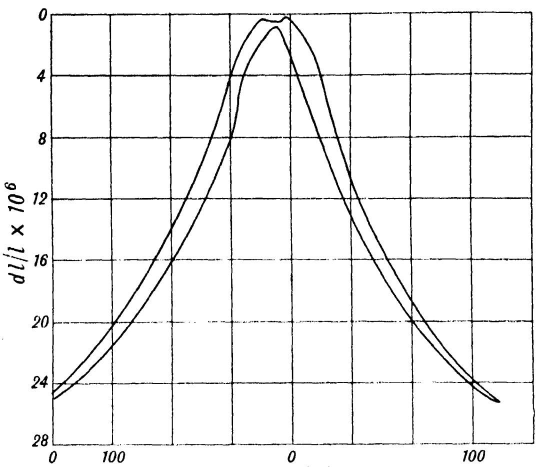


FIG. 77.—The Effect of the Magnetic Field Strength on Magnetostriction.

I	855	1711	3421	5089	8513 grms. per sq. mm.
$H=1{\cdot}14$ I_i	6·6	9·7	3·5	−4·1	−9·2
$H=1{\cdot}14$ I_c	−13·5	−32·2	−81·0	−99·4	−108·6
$H=364{\cdot}7$ I_i	−0·3	−0·6	−2·1	−4·1	−11·3

They also found that with a constant tension, the magnetization increases steeply in low fields, and after passing a point of inflexion, gradually approaches saturation. The effect of tension is large, and always to diminish magnetization. They also examined the effect of a twist, and of a combined twist and tension on the magnetization. In all cases the reciprocal nature of the changes of strains by magnetization and of the changes of magnetization by strain were established. For instance, magnetic elongation under constant tension and of magnetization under constant tension; of elongation by tension under a constant field, and the change of magnetization by tension under a constant field; of magnetic twisting under a constant couple, and magnetization under a constant twist; and of the change of rigidity under a constant field; and the change of magnetization by twist under a constant field.

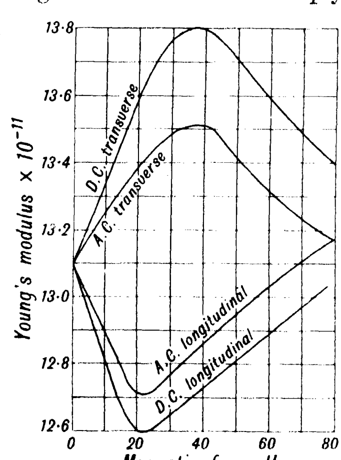


FIG. 78.—The Effect of a Magnetic Field on Young's Modulus.

W. Brown measured the effect of different magnetic fields, transverse and alternating, with direct and alternating currents of 50 to 150 cycles, on Young's modulus of

elasticity, E, in grams per sq. cm., with a load of 10^5 grms. per sq. cm.; the results, plotted in Fig. 78, are:

H			0	5	20	30	40	50	60	80
$E\times 10^{-11}$	Long.	D.C.	13·11	13·00	12·60	12·66	12·74	12·82	12·90	13·05
		A.C.	13·11	13·00	12·67	12·72	12·81	12·89	12·98	13·01
	Trans.	D.C.	13·11	13·20	13·57	13·74	13·80	13·72	13·59	13·39
		A.C.	13·11	13·18	13·37	13·47	13·52	13·43	13·33	13·17

Y. Masiyama found that with single crystals the longitudinal effect of magnetization is a contraction for all fields, and it is greatest in the direction of (100), next in the direction (110), and least in the direction (111). The transverse effect is just the reverse of the longitudinal effect. With a constant field, the variation of these effects with respect to the orientation is periodical, the period being 90°, 180°, and 60° for the planes (100), (110), and (111) respectively as in the case of magnetization. K. Honda and S. Shimizu's observations on the effect of temp. and magnetizing force, H, on the magnetostriction of nickel are summarized in Fig. 79. H. Masumoto gave:

H	3·0	10·8	52·6	115·5	179	307	500	629
$\delta l/l\times 10^6$	−0·89	−9·42	−24·21	−33·30	−38·42	−43·03	−46·22	−46·77

The subject was studied by S. R. Williams, A. Schulze, C. W. Heaps, B. Wedensky and J. Simanoff, E. Giebe and E. Blechschmidt, W. Möbius, F. Lichtenberger, W. Fricke, R. Gans and J. von Harlem, P. McCorble, F. C. Powell, J. S. Rankin, D. S. Scheinberg, E. Fromy, K. C. Black, A. W. Smith, J. M. Ide, A. B. Bryan and C. W. Heaps, S. Bidwell, J. A. Ewing and G. C. Cowan, H. Tomlinson, P. Curie, A. Gray and A. Wood, E. T. Jones, W. Leick, R. Beattie, H. A. Pidgeon, P. E. Shaw and S. C. Laws, H. Nagaoka and S. Kusakabe, H. Nagaoka and K. Honda, K. Honda and S. Shimizu, L. W. McKeehan, C. G. Knott, C. G. Knott and P. Ross, K. Nakamura, G. Scharff, and J. Russell. W. Brown compared the effect of transverse and longitudinal magnetic fields, continuous and alternating, on the magnetostriction of nickel, and found:

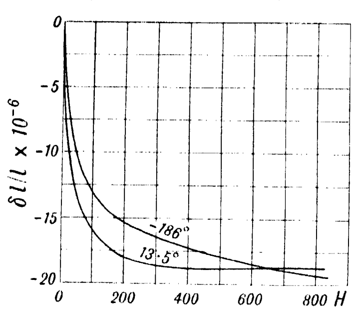


Fig. 79.—The Effect of Temperature and Magnetizing Force on the Magnetization of Nickel.

H			20	40	60	80	100	200
$\frac{dl}{l}10^6$	direct	Long.	11	19	25	30	—	42
		Trans.	3·0	9·5	11·0	8·0	6·5	3·5
	altern.	Long.	12	21	282	34	—	52
		Trans.	5·0	11·5	13·5	10·5	8·5	5·0

The results are plotted in Fig. 80. There is a steady contraction with both alternating and direct currents in a longitudinal field. For both direct and alternating transverse magnetic fields, nickel expands to a maximum and then diminishes gradually for high fields. The maximum expansion for both direct and alternating transverse fields takes place in the same field strength of about 50 c.g.s. units. He also measured the effect with alternating currents with 50 to 150 cycles; and also the effect with wires of different rigidities. R. Jouaust studied the subject. For N. S. Akuloff's observations, *vide supra*. J. S. Rankin studied the effect of overstrain on the magnetostriction; M. Kersten, and R. Becker and M. Kersten, the effect of large stresses on the magnetization of nickel; C. S. Yeh, the effect of hydrostatic pressure; and C. V. Kent and B. J. Babbitt, the effect on a vibrating nickel wire.

According to S. R. Williams, with cold-rolled nickel, the change in length in a magnetic field decreased asymptotically to the axis of hardness and as the alignment

of the crystals became complete. No initial lengthening was observed, and it was concluded that there is also no Villari reversal point for nickel. The area of the hysteresis curves taken on the strips increased with increasing hardness. The specific resistance first decreased and subsequently increased with the hardness. The mechanism for change of length must have some factor distinctly different from that which produces the other magnetic phenomena. The results of Y. Masiyama for single crystals are summarized in Fig. 81. According to W. L. Webster the rôles of the (100)- and (111)-axes are interchanged from what they are with iron, and the distortion produced by the increase of uniformity becomes a contraction. The two kinds of distortion can, however, still be separated. It is particularly noticeable that there is relatively little change in length for the (100)-axis below intensities 300 c.g s. units of magnetization. For the (100) direction, the effect of the deviation term is shown by the sharp increase in slope at 420 c.g.s. units, where from the I/H curve it is clear that the deviation is first brought into play. S. R. Williams and R. A. Sanderson studied the changes in length produced by a magnetic field of 58·8 gauss on samples of nickel of different degrees of hardness, and the results are summarized by the dotted curve in Fig. 75. E. Bauer studied the relation between the dilation and the magnetization of nickel.

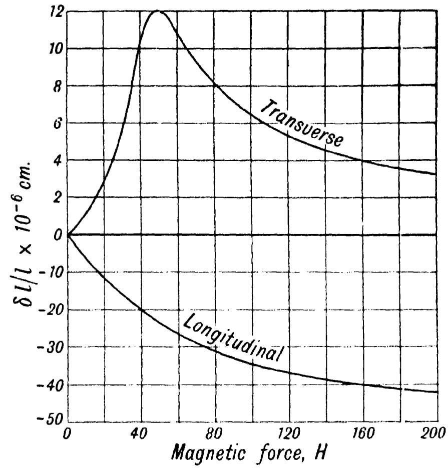


FIG. 80.—Magnetostriction of Nickel in Transverse and Longitudinal Magnetic Fields.

K. Honda and T. Tanaka found that the effects of a magnetic field on the elastic modulus, E, and the coeff. of rigidity, K, of nickel are :

H . .	16·4	57·7	108	165	266	363	403
$\delta E/E \times 10^2$	0·073	0·392	1·13	1·62	2·15	2·50	2·64
H . .	10·2	33·0	63·0	103	186	243	359
$\delta K/K \times 10^2$	0·18	0·70	1·62	3·06	4·93	5·72	6·97

W. Brown measured the subsidence of torsional oscillations of nickel wires when subjected to the influence of direct and alternating currents with magnetic fields up to 800 c.g.s. units. With a soft nickel wire both direct and alternating current fields increase the damping of the torsional oscillations. He also measured the fatigue of nickel wire when subjected to the influence of longitudinal and transverse alternating magnetic fields. The maximum fatigue due to a transverse, alternating field is about 8·5 per cent. less than is the case with a longitudinal, alternating field, and it takes about double the time to attain the maximum. J. W. Peck and R. A. Houstoun, C. V. Kent and B. J. Babbitt, A. Gray and A. Wood, R. Becker and M. Kornetzky, A. Drigo measured the effect of a variable magnetic field on the internal friction, or the damping of the torsional oscillations of nickel wire; W. Möbius, the effect on the torsion modulus; F. von Schmoller, the **Matteucci effect** with nickel and iron—that is, the induction of a transverse e.m.f. on changing the longitudinal magnetization of a wire under torsion; and C. Williams, the effect on the thermal expansion.

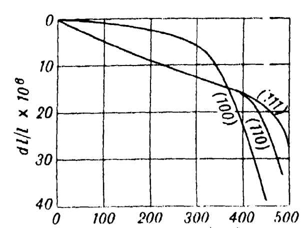


FIG. 81.—The Magnetostriction of Single Crystals of Nickel.

A. Perrier and C. E. Borel, W. Heisenberg, J. Dorfman, L. Cambi and L. Szegö, R. Gans and co-workers, D. M. Bose, G. Foëx and B. Kessler, W. Klemm and co-workers, L. Néel, D. Rozansky, R. Schlapp and W. G. Penney, R. W. Roberts, and J. R. Ashworth discussed the theory. J. R. Ashworth studied the relations between the magnetic and thermal constants. G. Schmaltz found that with a field strength of 1200 c.g.s. units, the heat conductivity of nickel decreases in the axial direction as opposed to the equatorial direction to the extent of about 5 per cent. The effect of a magnetic field on the electrical resistance of nickel has been examined by S. Kaya, G. Barlow, and N. S. Akuloff, and the subject has been previously discussed. W. Sucksmith and L. F. Bates, O. Dahl and J. Pfaffenberger, and S. J. Barnett studied the gyromagnetic effect which amounts to about 0·501—*vide* iron; D. M. Bose and P. K. Raha, the photomagnetic effect; F. Ehrenhaft, the magnetophoresis and electrophoresis of nickel; A. Perrier and C. E. Borel, the longitudinal magnetic effects of electric currents; W. H. Ross, the effect of magnetization on the thermoelectric force; H. Broili, the thermomagnetic effect in a longitudinal magnetic field; and F. Wever, the atomic arrangement of magnetic and non-magnetic nickel.

According to W. Gerlach, if a fall of temp. takes place in a ferromagnetic body, then an electromotive force appears between its ends in a homogeneous magnetic field whose lines of force run parallel to the direction of the fall of temp. This e.m.f. shows about the same degree of dependence on the magnetization as the change of resistance. If a piece of nickel wire is kept at a temp. T_1 of about 20°, and if the temp. T_2 of the other end is raised, then a magnetic field parallel to the lines of fall of temp. creates an e.m.f. which steadily increases and reaches an

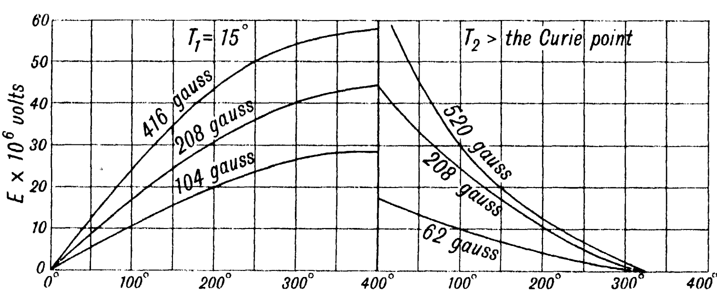


FIG. 82.—The Thermomagnetic Effect as a Function of Temperature.

approximately constant value as soon as T_2 exceeds the Curie point. If T_1 be now increased while T_2 is kept at any given temp. above the Curie point, then the e.m.f. created by the magnetic field decreases and becomes zero as soon as T_1 is equal to the temp. of the Curie point. The e.m.f. remains constant while the field effect remains constant. It is independent of the course of the fall of temp. and only dependent on the difference of temp. This effect is obviously connected in the same way with the magnetization as is the change of resistance at constant temp. W. Gerlach also found the relation between the e.m.f. and the intensity of magnetization; and showed that the small hysteresis corresponds with the hysteresis of the resistance to change. S. C. Tao and W. Band, and T. Kousmine studied the subject.

P. Weiss and co-workers gave 3 and 4 for the atomic moment of nickel, and observations on the subject were made by J. Dorfman and co-workers, A. Wolf, G. Sadron, E. C. Stoner, and H. Fahlenbruch. H. Sachsse, E. Vogt, and C. Sandron discussed the at. moment of nickel when alloyed with chromium and manganese. S. Datta, L. Cambi and E. Tremolada, U. Dehlinger, R. B. Janes, and D. M. Bose and P. K. Raha discussed the magnetic properties of the nickel salts (*q.v.*); and S. S. Bhatnagar and co-workers, the change from paramagnetism to diamagnetism when the salts are adsorbed on charcoal.

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§ 7. Chemical Properties of Nickel

Entre les propriétés chimiques du nickel et du cobalt, nous ne savons établir qu'une différence de degré.—H. MOISSAN.

F. Fischer and co-workers,[1] V. Kohlschütter, J. C. Stimson, and W. Frankenburger and co-workers, spluttered electrodes of nickel in liquid **argon,** but observed no sign of chemical combination. A. Sieverts and E. Bergner also observed that argon and **helium** do not show a measurable solubility in nickel. V. Lombard studied the permeability of nickel to argon and helium. L. R. Ingersoll and J. D. Hanawalt thought that compounds of helium and argon with nickel were formed by spluttering the metal in these gases, but they later showed that this is not the case. When nickel is cooled in the presence of helium it does not show the absorption phenomenon characteristic of the clean-up, with hydrogen. The subject was studied by V. Lombard, and J. M. Jackson. E. Rupp found adsorbed argon had no perceptible effect on the space-lattice of nickel. G. I. Finch and J. C. Stimson studied the electrical charge of the metal when adsorbing argon.

W. Schlenk and T. Weichselfelder [2] treated anhydrous nickel chloride with an ethereal soln. of magnesium phenyl bromide and obtained a dark brown, colloidal soln. of nickel which absorbed **hydrogen** rapidly, and the nickel was thereby precipitated as a black sediment, leaving the liquid clear. The vol. of hydrogen absorbed agrees with NiH_4, but when the black product is dried in a current of hydrogen, **nickel dihydride,** NiH_2, remains. When this product is treated with alcohol, it begins to evolve hydrogen, but it is stable in contact with ether. T. Weichselfelder and B. Thiede did not regard NiH_4 as a chemical individual. M. Kossodo observed the conditions under which ethylene is transformed into ethane by the action of nickel dihydride in the presence of ether. G. F. Hüttig studied the relationship of the hydride to other hydrides.

H. T. Wensel and W. F. Roeser observed that before repeated fusion in vacuo, the gas content of 99·94 per cent. nickel was 0·001 per cent. of oxygen ; 0·0002 per cent. hydrogen ; and no nitrogen ; whilst afterwards there were present 0·008 to 0·015 per cent. oxygen ; 0·0002 per cent. hydrogen ; and 0·004 per cent. nitrogen. The subject was studied by W. Hassenbruch, A. Kemper, S. W. Ptitzyn and L. M. Fink, G. A. Grinberg, J. Maslakovetz, and H. Nishimura. According to P. D. Merica and R. G. Waltenberg, nickel remains malleable after it has been melted and solidified in hydrogen. In 1869, F. M. Raoult found that when commercial nickel is used for 12 hrs. as cathode in acidulated water, it absorbs 165 vols. of hydrogen per unit vol. of metal. A. Villachon and G. Chaudron, W. A. Lazier and H. Adkins, J. J. Ackworth and H. E. Armstrong, W. Ipatéeff, and R. Böttger also observed the occlusion of hydrogen by nickel ; and L. Troost and P. Hautefeuille showed that sheet nickel, employed as cathode in acidulated water, can absorb up to 40·0 vols. of hydrogen, and when heated in hydrogen it absorbs 16 vols. of the gas. Nickel powder obtained by reducing the oxide in hydrogen absorbed 100 vols. of hydrogen, and G. Neumann and F. Streintz found that the powder obtained by reducing the oxalate absorbed 17·5 vols. M. Bellati and S. Lusanna found that impure nickel wire employed as cathode absorbed 100 vols. of hydrogen. W. Hempel and H. Thiele observed no occlusion with nickel reduced from the oxide of a high degree of purity, but G. P. Baxter found that the spongy nickel, reduced from the purified oxide, absorbed 3·0 to 10·7 vols. of hydrogen ; and M. Mayer and V. Altmayer observed that nickel reduced from the oxide by hydrogen at 360° to 560°, and 360 to 440 mm. press., absorbed 50·5 vols. W. A. Lazier and H. Adkins found that 100 grms. of nickel reduced by hydrogen absorbed 70 c.c. of hydrogen under standard conditions, and 205 c.c. when the metal had been reduced by alcohol. The occlusion of hydrogen by nickel was studied by W. Baukloh and H. Kayser, A. F. Benton and T. A. White, W. Frankenburger and co-workers, J. Hagenacker, F. C. Lea, N. I. Nikitin, J. Pace and H. S. Taylor, W. Rohn, H. O. von Samson-Himmelstjerne, J. C. Stimson, W. Hessenbruch, I. J. Smittenberg, L. L. Hasse and B. Schenck, G. F. Hüttig, D. Alekséeff and L. Savinia, H. N. Huntzicker and L. Kahlenberg, S. Iijima, R. Klar, E. W. R. Steacie, E. G. Insley, and A. Villachon and G. Chaudron. W. Frankenburger and co-workers studied the absorption of hydrogen by the highly dispersed metal.

W. Römmler found that electrolytic nickel at room temp., and 740 to 760 mm. press., absorbed from 4·3 to 13·6 times its vol. of hydrogen. The hydrogen content of electrolytic nickel increases as the acidity of the electrolyte—a soln. of nickel sulphate or chloride—is decreased, and it decreases as the temp. of the electrolyte is raised. A. Sieverts and W. Krumbhaar found that the amount of hydrogen absorbed by solid and molten nickel is proportional to the sq. root of the hydrogen press., that the absorption of gas is greater with the molten metal, so that during the solidification of the metal in air, spitting may occur—**3.** 22, 7 ; and that 100 grms. of 98·5 per cent. nickel wire, Fig. 83, absorbed S mgrm. of hydrogen at different temp., and 760 mm. press. :

	212°	520°	822°	1123°	1300°	1400°	1451°	1465°	1600°
S .	0·16	0·39	0·72	1·148	1·320	1·539	m.p.	3·50	3·87

G. Borelius gave the solubility S of hydrogen in nickel at $T°$ K. to be $S=ae^{1920/T}$, where a is a function of the temp., and at a high temp., a has nearly the same value for all metals. B. C. Hendricks and R. R. Ralston represented the rate of diffusion of hydrogen, D, through nickel by $D=kp^{\frac{1}{2}}T^{\frac{1}{2}}e^{-q/4T}$, where p and T, respectively, denote the press. and absolute temp., whilst q and k are constants ; W. R. Ham modified the equation ; and V. Lombard gave $D=k10^{at}$, but B. C. Hendricks and R. R. Ralston did not get good results with this equation, or with H. M. Ryder's equation, $D=kT^{b}$. V. Lombard found that the rate of diffusion of hydrogen through nickel is independent of the presence of nitrogen, and it varies

inversely as the thickness in accord with Fick's law. Expressing the results in terms of D mgrms. of hydrogen diffusing per sq. metre of metal 1 mm. thick, per hour, B. C. Hendricks and R. R. Ralston found:

	760 mm.				390·6 mm.			115 mm.		
	478°	570°	678°	798°	471°	597°	677°	498°	658°	719°
D . .	34·2	88·6	176·7	369·2	28·7	81·7	133·4	23·1	65·4	94·2

Observations were made by D. Alekséeff and L. Savinia, H. G. Deming and B. C. Hendricks, A. W. Gauger, W. A. Lazier and H. Adkins, and C. J. Smithells. T. A. White and A. F. Benton studied the absorption of hydrogen by nickel poisoned by carbon monoxide.

G. Tammann and J. Schneider's observations on the rate of absorption of hydrogen by nickel at different temp. are summarized in Fig. 84. The metal

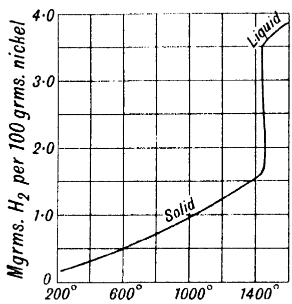


FIG. 83.—The Solubility of Hydrogen in Nickel.

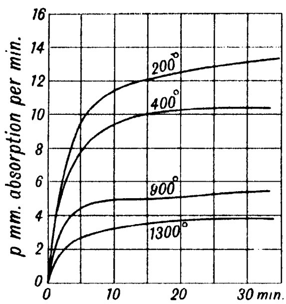


FIG. 84.—The Rate of Absorption of Hydrogen in Nickel.

absorbs hydrogen at 200° to 300° more rapidly, and to a greater extent, when hard than when soft, but the reverse holds for electrolytic hydrogen. The results for the cold-worked, or hard metal with a cathodic surface area of 4·79 sq. cm., thickness 0·288 mm., and a current of 25 milliampères in 1·1N-NaOH, are shown in Fig. 85. A. F. Benton and T. A. White found that, at a given press., the absorption of hydrogen—expressed in c.c. at 0° and 760 mm.—by 23·10 grms. of nickel, is

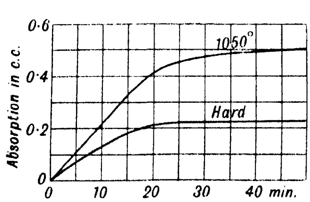


FIG. 85.—The Absorption of Electrolytic Hydrogen by Nickel.

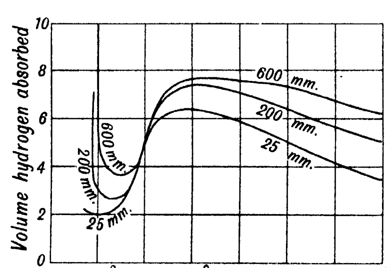


FIG. 86.—The Effect of Pressure on the Absorption of Hydrogen by Nickel.

relatively large at very low temp.; it then decreases to a minimum at —200° to —175°, dependent on the press.; and then rises to a maximum at about —100° as indicated in Fig. 86. At 600 mm. press., the adsorption is independent of the temp. between —110° and 0°, showing that a saturated single layer of molecules is probably formed.

According to J. D. Hanawalt and L. R. Ingersoll, when nickel is baked at 200° to remove surface gas, and allowed to cool at a press. of about 0·1 mm. no decrease of press. occurs until a certain critical temp. is reached, when rapid absorption occurs. This "clean up" phenomenon is limited to hydrogen; it holds for nickel

spluttered in hydrogen, helium, and argon. The critical temp. depends on the previous baking of the metal. If the baking of the film has been thorough so as to produce normal and complete crystallization, the critical temp. may be 400°, but if the baking has been slight, the critical temp. may be 100°. The absorbed hydrogen does not affect the crystal lattice. The amount of hydrogen absorbed may be many times—possibly fifty—that required for a monomolecular layer in the ordinary sense. The process of absorption is a kind of solution, which occurs at a temp. dependent only on the state of aggregation, and thus the phenomenon differs from the absorption studied by A. Sieverts, and G. Borelius. The gas seems to be located in the intercrystalline region. The subject was discussed by A. W. Gauger and H. S. Taylor, N. I. Nikitin, W. A. Lazier and H. Adkins, I. J. Smittenberg, and J. W. Terwen. C. G. Fink and co-workers observed H^1 diffuses more quickly than H^2. W. H. Melville compared the action of the two isotopes on nickel.

H. C. H. Carpenter found that the brittleness which develops when nickel is employed for the resistance wires of electrical furnaces, is due to the absorption of gases by the wires. L. Guillet and J. Cournot studied the effect of hydrogen on the mechanical properties of the metal, *vide* iron, **13.** 66, 23; G. Tammann and J. Schneider, the effect of the crystalline structure of the metal; and G. Tammann, the effect of cold-work on the absorption of hydrogen. B. Foresti gave 11·4308 Cals. for the heat of absorption of hydrogen by nickel reduced from the oxide by hydrogen at 300°; and R. A. Beebe and H. S. Taylor gave 13·35 to 21·00 Cals. per gram-atom of nickel. Observations were made by C. F. Fryling. E. Rupp studied the optical properties of the adsorption film; G. I. Finch and J. C. Stimson, the electrical state of the metal during the adsorption of gases; T. Skutta, and A. Coehn and K. Sperling, the effect of the adsorbed hydrogen on the electrical resistance; A. Janitzky, and F. P. Bowden and E. K. Rideal, the electrolytic behaviour of a cathode of nickel; J. H. Wolfenden, and G. B. Kistiakowsky, the ionization potential of the adsorbed hydrogen; J. E. Nyrop, P. H. Emmett and R. W. Harkness, and G. I. Finch and J. C. Stimson, the electrical state of the surface; J. A. Kendall, the cell formed with a plate of nickel through which hydrogen is passing; A. Farkas, H. Busch, K. F. Bonhoeffer and co-workers, K. Fajans, G. Tammann, and H. S. Taylor and A. Sherman, the parahydrogen transformation on the surface of nickel; and J. Horiuchi and M. Polanyi, and O. Schmidt, the catalytic property of nickel in hydrogenations.

The absorption of hydrogen involves a rapid primary absorption, and a much slower secondary absorption. According to one hypothesis—*vide* nickel—the primary process is a true surface adsorption, and the secondary process involves a gradual penetration by diffusion or solution of the gas into the interior of the metal. H. S. Taylor assumed that two adsorption processes are involved, one with molecular and the other with atomic hydrogen. The subject was studied by E. B. Maxted and N. J. Hassid, A. A. Shukhovitsky, and K. S. Ablezova and S. Z. Roginsky. C. Y. Meng and co-workers, O. I. Leypunsky, A. W. Gauger, M. V. Tolyakoff, T. Franzini, and N. Koboseff and N. I. Nekrassoff found that hydrogen emitted from a state of occlusion in nickel is probably atomic because it reduces a suspension of tungstic oxide. This subject is discussed in connection with platinum, and palladium. L. S. Ornstein and A. A. Kruithof found that the oxidation of the surface reduces the rate of re-combination of the atoms of occluded hydrogen. L. S. Ornstein and A. A. Kruithof observed that the re-combination of hydrogen atoms into molecules proceeds faster with oxidized nickel than it does with a nickel surface.

According to J. B. Richter,[3] and U. R. Evans, nickel does not oxidize in **air** at ordinary temp. even though the air be humid. The metal was found by H. J. French to be resistant to, but not proof against, moist, salty atmospheres. W. H. J. Vernon found that in the "fogging" of nickel when exposed to air a film of nickel sulphate with a small proportion of sulphuric acid is formed, and in this state, the film may

be removed by wiping with a cloth. If not removed, the action proceeds further, the sulphuric acid reacts with the nickel, and the film is converted into a basic sulphate which can be removed only by abrasion—*vide infra*, the action of sulphur dioxide. J. Jahn observed that during one hour's exposure:

	Moist Air		Dry Air	
	199°	300°	198°	297°
Nickel	5346·4	5347·4	5346·4	5353·8 mgrms.
Change in weight . . .	0	−0·6	−0·1	−0·5 mgrm.

L. Thompson found that when nickel is exposed to air, it gradually acquires a yellowish film; and C. D. Tourte showed that when the metal is heated, it gradually tarnishes and acquires an iridescent surface film, like steel, whilst at a red-heat, R. Tupputi noted that it becomes covered with a greenish-grey oxide, and is ultimately converted into a brown, brittle mass, which is either a suboxide, or a mixture of the monoxide with metallic nickel. The latter alternative is the more probable one since the product is attracted by a magnet. P. Oberhoffer studied the subject. H. St. C. Deville also observed that when the metal is melted in air, it oxidizes only superficially, and furnishes a kind of hammer-slag—*vide* iron, **13.** 66, 29.

N. B. Pilling and R. E. Bedworth found that nickel oxidizes very slowly, and between 800° and 1000°, the quantity of oxygen, w, forming the oxide in the time t, is given by the equation: $w^2=kt$, where k is a constant. This shows that the quantity of oxygen combining with the metal is proportional to the sq. root of the time of exposure. A cross-section of an oxidized sheet of nickel did not show any intercrystalline oxidation. N. V. Agéeff discussed the intercrystalline brittleness of nickel due to oxidation. N. B. Pilling and R. E. Bedworth observed that during the oxidation of the purified metal at 1000°, the circumferential tension increases so as to cause the oxide to peel off in scales spontaneously because the adhesion of the oxide to the metal is slight. Nickel of a low degree of purity oxidizes more rapidly than electrolytic nickel. The oxidation constant, k, of nickel is so related with the temp., T° K., that $k=0{\cdot}0_7 33T^{19{\cdot}0}$, and, at 800°, $k=0{\cdot}0_7 93$; at 900°, $k=0{\cdot}0_6 76$; and at 1000°, $k=0{\cdot}0_5 34$ in grams per sq. cm. per hour. Y. Utida and M. Saito observed that with a 2 hours' heating at 1170°, 1100°, and 1000°, nickel wires gained, respectively, 4·94, 4·24, and 1·88 mgrms. oxygen per sq. cm. M. Centnerszwer and H. Zyskowicz observed that air and **oxygen** do not act on nickel foil between 50° and 150°, but that there is a marked action on nickel powder. Blue nickel monoxide is formed at 280° to 290°. Nickel becomes slightly oxidized at 500°, and in 15 days, at 1000°, nickel will oxidize to a depth of about 0·001 in. G. Tammann estimated that, at 15°, dry oxygen would require 15 years to produce a visible film on nickel. F. H. Constable studied the interference colours produced by films developed in the oxidation of nickel between 300° and 500°; J. C. Stimson, G. D. Preston, G. Jung, A. M. Portevin, B. Bogitch, U. R. Evans and J. Stockdale, G. Tammann and W. Köster, G. Tammann and C. F. Marais, G. Tammann and G. Siebel, G. Tammann and E. Schröder, W. Köster, and H. J. French, the growth of oxide films, or tarnish films, on nickel; M. Fink and U. Hofmann, the growth of oxide films in air by friction on the metal; J. A. Hedvall and co-workers, the increase in the rate of oxidation of nickel at the Curie point; N. Krings, the equilibrium in the system; Fe–Ni–O; and J. C. Hudson, the effect of atm. corrosion on the breaking load on hard wires.

According to G. Magnus, nickel reduced by hydrogen at a gentle heat is pyrophoric; W. van Rijn said that nickel reduced from the oxalate in a strong current of hydrogen is not pyrophoric; and G. Tammann, and N. I. Nikitin found that nickel powder reduced below 370° from the oxalate is pyrophoric. G. Tammann and W. Boehme observed that nickel obtained by reducing the oxalate at 350°, inflames in air at −4° to −8°, and in oxygen at −10° to −8°. According to W. Ipatéeff, and H. Moissan, nickel reduced at 270° is oxidized by exposure to

ordinary air; if reduced between 270° and 280°, it is incompletely oxidized by dry air or oxygen only at 350°, and it is completely oxidized at 400°. Nickel is oxidized by moist oxygen at 300°, but it is scarcely attacked by dry oxygen at that temp. C. D. Tourte observed that nickel burns with the emission of vivid sparks when it is placed on a glowing coal fed with oxygen gas; and J. J. Berzelius added that when a nickel wire, with a piece of glowing charcoal at the end, is introduced into oxygen, the metal burns for a short time with the emission of sparks.

C. F. Schönbein found that nickel moistened with water, or very dil. sulphuric acid, and exposed to air, forms nickel hydroxide which liberates iodine from potassium iodide. H. O. Forrest and co-workers found that the initial corrosion of nickel by aerated water furnishes a curve, Fig. 87, similar to the curves for iron and of its alloys—*vide* corrosion, **13.** 66, 24. The curve, Fig. 87, shows the consumption of oxygen in c.c. per sq. dm., at different intervals of time; and the flattening of the curve indicates that a protective film is forming.

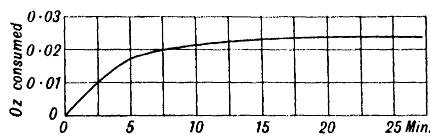


FIG. 87.—The Corrosion of Nickel by Oxygenated Water.

For the occlusion of oxygen, *vide supra*, hydrogen. W. W. Russell and O. C. Bacon gave 98 Cals. for the molar heat of absorption of oxygen by nickel. W. W. Russell and L. G. Ghering studied the subject.

N. B. Pilling and R. E. Bedworth said that a cross-section of an oxidized sheet of nickel does not show any intercrystalline oxidation. N. V. Agéeff, and M. Cook discussed the intercrystalline brittleness of nickel due to oxidation. P. D. Merica and R. G. Waltenberg found that the brittleness acquired by nickel which has been melted is not due to the presence of nickel oxide, for nickel remains malleable when it contains up to the eutectic proportion of oxygen, namely, 0·24 per cent. oxygen, or 1·1 per cent. nickel oxide; nor is malleable nickel which has been melted in an open crucible rendered non-malleable. The harmful element is sulphur—*vide infra*. Manganese, aluminium, and magnesium act as deoxidizers when they are added to the molten metal. The subject was discussed by G. Masing and L. Koch, and W. Köster.

R. Schenck and H. Wesseldonk observed that the activation of powdered nickel against oxygen is possible by heating the powdered metal with oxides of those metals which form solid soln. of a chemical compound with nickel oxide—*e.g.*, CaO, MgO, MnO, and Al_2O_3. W. A. Bone and R. V. Wheeler, D. R. Hughes and R. C. Bevan, G. Kröger, H. Remy, F. Thorén, A. F. Benton and P. H. Emmett, F. E. Smith, H. P. Cady and W. E. White, and R. P. Donnelly studied the catalysis of the hydrogen-oxygen reaction by nickel; and L. Kahlenberg, the activation of gases by nickel. C. Kelber found that nickel reduced from the carbonate at 410° has no action on a mixture of hydrogen and oxygen at ordinary temp., but if the carbonate, previous to reduction, be distributed over an inert substance, it catalyzes the reaction like colloidal palladium does. A. T. Larson and F. E. Smith, C. Sandonnini, and R. P. Donnelly studied the combination of hydrogen and oxygen on the surface of nickel wires; and W. H. Melville compared the effects with the two isotopes of hydrogen. According to M. Poljakoff, when hydrogen at 3 to 5 mm. press. is passed over nickel at 400° to 800°, no luminescence is observed, but if a small stream of oxygen or air is added at a point remote from the metal, a violet, green, or yellow luminescence occurs. The luminescence is not observed with a mixture of hydrogen and oxygen. F. E. Smith studied the activation of nickel by copper. W. Manchot observed that nickel reacts with **ozone** at 415°.

According to R. Tupputi, nickel does not decompose **water** at ordinary temp., but H. V. Regnault found that at a red-heat, the metal decomposes steam, forming a light, olive-green, crystalline oxide. G. Chaudron did not confirm this. A. Skapsky and J. Dabrowsky, and E. Neumann discussed the reaction: $Ni+H_2O \rightleftharpoons NiO+H_2$

—*vide infra*, nickel oxide. G. I. Finch and J. C. Stimson studied the electrical charge of the metal when adsorbing water vapour. M. Guichard, G. Tammann and W. Boehme, and T. Ihmori discussed the tendency of water to condense on a cold surface of nickel; and S. S. Bhatnagar and S. L. Bhatta, the tendency of water to evaporate from nickel surfaces. W. van Rijn observed that finely-divided nickel does not furnish hydrogen in contact with water, but it does so in contact with dil. hydrochloric or sulphuric acids; mercury has no perceptible influence on the result. C. F. Schönbein observed that if nickel is kept for a long time in contact with water and air, it acquires a green film of an oxide. M. Traube-Mengarini and H. Scala found that when nickel is in contact with water, it very gradually yields a colloidal soln. W. Merckens said that when nickel is exposed to moist air, it forms hydrogen dioxide more readily than is the case with cobalt or lead—for the attack by moist air, *vide supra*. R. J. McKay found that nickel is very susceptible to attack by mixtures of steam and carbon dioxide. R. Saxon observed the corrosion of a nickel anode in the electrolysis of water; N. M. Zarubin, the settling in water. According to W. P. Jorissen, 99·9 per cent. nickel retained its polish and gave no evidence of corrosion after being exposed for 4 weeks to the action of sea-water and air. W. M. Mitchell, H. Moore and E. A. G. Liddiard, F. Renaud, J. C. Hudson, and J. A. N. Friend examined the corrosion of nickel by sea-water; and W. G. Whitman and R. P. Russell, by oxygenated water. J. I. Crabtree and G. E. Matthews observed that water has no action on nickel. W. Guertler and T. Liepus found that nickel is attacked when exposed for 8 days to rain-water and air, sea-water, and sea-water and air, but not by 10 and 50 per cent. soln. of **sodium hydroxide** during 4 weeks; but it is attacked by a mixed soln. of sodium hydroxide and **hydrogen dioxide.** A. J. Hale and H. S. Foster observed that 0·2N-NaOH had no perceptible action on nickel after 28 days' exposure; and with N-NaOH, D. F. McFarland and O. E. Harder found that nickel lost 18·70 mgrms. per sq. in. in a week. T. Okamoto, and A. von Kiss and F. E. Lederer studied the subject. R. Krulla's observations are summarized in Fig. 88. R. J. McKay noted that nickel resists very well the attack by hot alkali lye, and that the resistance decreases with a rise of temperature. W. Dittmar, A. R. Miro and N. G. Morales, R. J. McKay, J. L. Everhart, W. Venator, R. Krzizan, A. Mermet, A. Quataroli, and L. l'Hôte observed that nickel is very resistant towards soln. of alkali hydroxide; and W. Venator found that it is very little attacked by fused alkali, although, at a high temp., A. Mermet found that the metal is attacked—*vide supra*, the uses of nickel. T. Wallace and A. Fleck found that sodium hydroxide attacks nickel very slightly in air between 350° and 600°, and that a crystalline substance, approximating $Na_2Ni_5O_{13}$, is formed. The attack is facilitated if the sodium hydroxide contains 5 per cent. of **sodium dioxide.** According to W. L. Dudley, the metal is readily attacked by molten sodium dioxide.

H. Moissan [4] found that when nickel is heated, it is attacked by **fluorine** and the other halogens. H. Rose observed that finely-divided nickel, when heated to low redness in a current of **chlorine,** burns with a vivid glow, forming yellow crystals of nickel chloride. W. Guertler and T. Liepus found that a sat. soln. of chlorine water slowly attacks the metal; and C. Willgerodt, that nickel can act as a catalyst in chlorinations in organic syntheses. J. B. Berthemot found that nickel filings are attacked by **bromine,** at a dull red-heat, forming yellow, micaceous scales of nickel bromide. A. Babinsky measured the rate of dissolution of nickel in bromine water. O. L. Erdmann noted the formation of nickel iodide when nickel and **iodine** are heated together in a sealed glass tube, or when the vapour of iodine is passed over the heated metal; but R. Hanslian observed no reaction at the temp. of boiling iodine. R. G. van Name and co-workers studied the rate of dissolution of nickel in an aq. soln. of iodine and potassium iodide. G. Tammann discussed the formation of surface films by exposure to the vapour of iodine. H. E. Fierz-David

found that unlike iron, nickel, in association with iodine, is not a satisfactory catalyst in the chlorination of benzene derivatives.

P. Schützenberger observed that some nickel is volatilized, presumably as chloride, when **hydrogen chloride** is passed over the metal at dull redness. The reaction was studied by P. Junius. G. Gut found that hydrogen chloride does not attack nickel reduced from the chloride at 210°, whilst the metal reduced from the oxide is attacked at that temp. K. A. Hofmann and co-workers gave for the relative rates of attack by hydrogen chloride at 300° Fe>Ni>Cu>Ag>Hg. R. Tupputi observed that nickel dissolves very slowly in dil. **hydrochloric acid** with the evolution of hydrogen and the formation of nickelous chloride. W. van Rijn made similar observations, and W. Guertler and T. Liepus found that the attacks by 10 and 30 per cent. hydrochloric acid were perceptible within 8 hrs. A. J. Hale and H. S. Foster observed that the losses in weight, in grms. per sq. dm., by polished nickel at 17° to 20° in 500 c.c. of 0·2N-HCl were 0·25 grm. in 7 days with the soln. renewed daily, and 0·45 grm. in 28 days when the soln. was not renewed. D. F. McFarland and O. E. Harder found that with N-HCl, nickel lost 207 mgrms. per sq. in. per week; and W. Rohn, that with 10 per cent. hydrochloric acid, unannealed nickel lost 0·025 grm. per sq. dm. in 24 hrs. with cold acid, and 0·47 grm. per sq. dm. in 1 hr. with the hot acid; the corresponding numbers for the annealed metal were, respectively, 0·04 and 1·51 grms. per sq. dm. R. Irmann found that when 10N-HCl, or 32 per cent. hydrochloric acid, acts on nickel at 95°, the loss is at the rate of 106 mgrms. per sq. cm. per hour. The action of acids was studied by B. Bogitch, W. Guertler and B. Blumenthal, M. Hansen, L. l'Hôte, W. P. Jorissen, R. J. McKay, R. Krulla, P. D. Merica, H. L. Olin and R. E. Wilkin, H. S. Rawdon and M. G. Lorentz, A. Rohde, R. A. Rohrman, T. K. Rose and J. H. Watson, B. Setlik, C. Tissier, W. H. V. Vernon, and H. F. Whittaker; C. L. Hippensteel, the inhibition of the action by iodine. R. Krulla's observations are summarized in Fig. 88. Illumination generally accelerates the rate of dissolution of nickel in hydrochloric acid. H. J. Prins found that the presence of nitrobenzene accelerates the dissolution of nickel in acids; and E. Salkowsky, that the presence of hydrogen dioxide also accelerates the attack by the acid—the action is here attributed to the presence of some free chlorine. A. Coppadoro found that the current-yield in the dissolution of nickel in 15 per cent. hydrochloric acid, under the action of an alternating current, is high as it is also in the case of sulphuric acid—*vide infra*. Very little chlorine is evolved during the electrolysis. L. V. Pisarzhevsky, and M. A. Rozenberg and V. A. Yuza observed that a magnetic field retarded the rate of dissolution of nickel in acids.

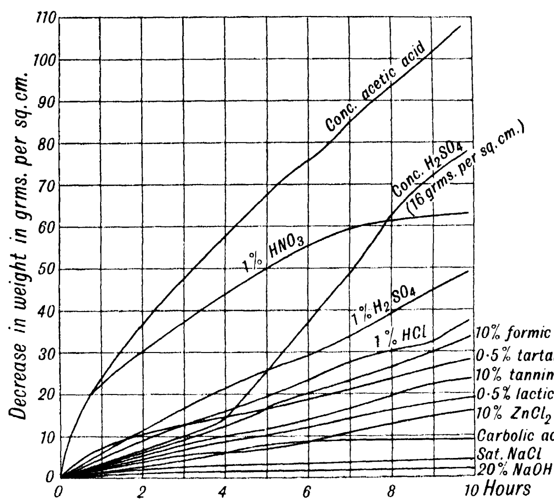


FIG. 88.—The Dissolution of Nickel in Various Solutions.

W. S. Hendrixson found that nickel is rapidly attacked by 2N-**chloric acid** at 50°; and A. Coppadoro, that in the alternating current electrolysis with a soln. of **sodium chlorate** as electrolyte, the nickel electrodes become almost perfectly passive. G. N. Quam studied the corrosive action of **hypochlorite** on nickel.

O. F. Hunziker and co-workers, and A. D. White noticed that a freshly-prepared soln. of calcium hypochlorite, of sp. gr. 1·04, gives off oxygen and chlorine when in contact with nickel, and nickelous hydroxide and chloride are formed.

E. Schürmann,[5] E. V. Britzke and A. F. Kapustinsky, and W. Guertler studied the affinity of **sulphur** for nickel. According to J. L. Proust, and H. Rose, when a mixture of nickel and sulphur is heated, the elements unite with incandescence to form nickel sulphide. I. P. Podalsky and N. M. Zarubin found that Ni_2S is formed below 600°, and Ni_3S_2, above 600°. According to P. D. Merica and R. G. Waltenberg, the ill-effects on the malleability of nickel, usually ascribed to oxygen, are really due to sulphur. The presence of 0·005 per cent. of sulphur is sufficient to reduce the malleability of the furnace-refined metal. The sulphur forms nickel sulphide, which is present as a eutectic, and surrounds the nickel crystals with a film which renders them brittle. As indicated in connection with the purification of the metal, T. Fleitmann recommended the addition of 0·05 to 0·125 per cent. of magnesium to molten nickel before casting to remove sulphur; and he also found manganese is a desulphurizer. In the case of magnesium, the insoluble sulphide which is formed is disseminated throughout the solid metal. The subject was studied by M. Cook, and B. Bogitch, whilst F. A. J. Fitzgerald and G. C. Moyer discussed the deterioration of nickel resistors by sulphur; and E. V. Evans and H. Stanier, the removal of sulphur from coal gas by a nickel catalyst.

According to J. Jahn, the action of **hydrogen sulphide** on approximately 3570 mgrms. of nickel, at different temp. for an hour, resulted in:

	100°	154°	203°	259°	313°	413°
Gain in weight .	0·7	0·5	2·5	5·3	13·5	29·9 mgrms.

H. Gruber exposed pieces of nickel, 60×12×12 mm., to the action of the gas for an hour, and found the gain in weight at 700° and 800° to be, respectively, 9·7 and 35 grms., but at 900° and 1000°, the pieces were destroyed. U. R. Evans observed that nickel becomes black when exposed over water saturated with hydrogen sulphide. E. Rupp studied the optical properties of the film produced by hydrogen sulphide; and W. Köster, the intercrystalline brittleness developed by exposing the metal to the gas. E. Priwoznik found that **ammonium polysulphide** darkens the colour of nickel, and that the black sulphide dissolves in the liquid. W. Guertler and T. Liepus found that nickel is attacked within 14 days by 10 and 50 per cent. soln. of **sodium sulphide,** and by a 4 per cent. soln. of sodium sulphide containing 8 per cent. of sodium hydroxide. E. Beutel and A. Kutzelnigg studied the surface films produced by heating nickel in contact with the **metal sulphides**—copper, silver, mercury, and lead. H. A. Krebs observed the catalytic action of nickel on the oxidation of alkali sulphides. A. Gautier and L. Hallopeau found that nickel monosulphide and hemisulphide are formed by the action of the vapour of **carbon disulphide** on nickel at a white-heat.

H. E. Patten, L. Vernitz and A. Kudinova, and E. H. Harvey found that nickel is very little affected after standing a year in contact with **sulphur monochloride,** and N. Domanitsky added that the attack is very slow, if it occurs at all. F. Wöhler, A. Baudrimont, and H. Feigel studied the action of sulphur monochloride. E. H. Harvey said that the action of sulphur monochloride, during a year's action at room temp., is small. H. E. Patten showed that **thionyl chloride** has no perceptible action on nickel. J. Uhl observed that **sulphur dioxide** forms some nickel sulphide when passed over the heated metal. L. Meyer studied the oxidation of the gas with a nickel catalyst. J. Jahn observed that on exposing about 3570 grms. of nickel to sulphur dioxide for an hour:

	100°	152°	202°	253°	300°	417°
Gain in weight .	0·0	0·1	0·1	0·2	0·2	5·5 mgrms.

According to W. Köster, when nickel is heated in an atmosphere containing sulphur dioxide the intercrystalline corrosion is shown to be due to the formation of the nickel-nickel sulphide eutectic which penetrates into the metal along the grain

boundaries. The rate of penetration increases with the temperature up to 800°, and once a quantity of the sulphide is formed subsequent annealing in an atmosphere free from sulphur causes further penetration. The sulphide being hard and brittle renders the whole of the metal brittle and leads to intercrystalline fracture when the metal is worked. P. Neogi and B. B. Adhicary observed that hydrogen sulphide is formed when a mixture of sulphur dioxide and hydrogen is passed over heated nickel or nickel nitrate. R. Schenck and E. Raub observed that nickel cobalt powder obtained by reduction of the formate with hydrogen reacts readily with sulphur dioxide, yielding cobalt sulphide and oxide, and the action is irreversible, at least below 1050°. The reaction $CoSO_4+4Co=4CoO+CoS$ proceeds to completion at 525° and is also irreversible, but the reaction $3CoSO_4+CoS\rightleftharpoons4CoO+4SO_2$ is reversible, provided that the solid reactants are in an extremely fine state of subdivision. The decomposition of cobalt sulphate by heat first becomes appreciable at about 900° and is complete after prolonged heating at 970°. Nickel reacts rapidly with sulphur dioxide at 550°, but equilibrium is established only after many days, complete conversion into nickel oxide and monosulphide being effected. The equilibrium is univariant, as there are three solid phases, but by removing part of the sulphur dioxide one of these disappears and the equilibrium becomes bivariant. From a consideration of the equilibrium diagram and from measurements of the sulphur dioxide pressure the three phases appear to be nickel oxide, nickel sulphide, and the γ solid solution ; with low pressures of sulphur dioxide the nickel sulphide phase disappears. The reverse reaction with the formation of nickel from nickel oxide and sulphide proceeds only as far as the solid solution phase below the m.p. (about 1400°) ; bundles of fine hair crystals of this phase, or possibly of Ni_3S_2, can be seen throughout the reacting mass in the early stages of this reaction. U. R. Evans found that nickel becomes black in a couple of days when it is exposed over water saturated with sulphur dioxide, and G. H. McGregor and J. W. Stevens, and O. Bachmann and W. Köster also studied the action of sulphurous fumes on nickel. According to W. H. J. Vernon, the fogging of nickel is partly due to the presence of suspended particles of sulphates in the air, but the presence of sulphur dioxide produces fogging much more rapidly owing to the catalytic oxidation of this gas to sulphuric acid. Light accelerates the formation of films ; and in darkness, the rate is about half what it is in sunlight. Fogging is inhibited by previous exposure of the nickel to air containing hydrogen sulphide, and almost completely by exposure to stagnant air at room temp. Annealing the metal at 225° to 350° has no effect on the rate of fogging. I. E. Adaduroff and K. I. Brodovitsch studied nickel precipitated on silica gel as a catalyst in the oxidation of sulphur dioxide. M. J. Fordos and A. Gélis, C. Geitner, P. Schweitzer, and M. Berthelot observed that in the action of **sulphurous acid** on nickel some sulphide and sulphur are formed as by-products. O. Bachmann and W. Köster studied the subject ; and E. M. Mrak and W. V. Cruess, the action of fruit juices treated with sulphur dioxide.

R. Fink discussed the affinity of nickel for **sulphuric acid.** R. Tupputi, and M. Berthelot found that nickel dissolves very slowly in dil. sulphuric acid with the evolution of hydrogen, and the formation of nickelous sulphate ; but with the conc. acid, some sulphur dioxide is also formed. W. Guertler and T. Liepus found that with 10 per cent. acid, and 20 per cent. acid saturated with sodium sulphate, there was an appreciable action in 8 hrs. J. I. Crabtree and G. E. Matthews observed that 5 per cent. sulphuric acid corrodes nickel at the rate of 0·69 grm. per 100 sq. in. per day. A. J. Hale and H. S. Foster observed the losses in weight per sq. dm. of polished nickel at 17° to 20° in 500 c.c. of $0{\cdot}2N\text{-}H_2SO_4$ were 0·25 grm. in 7 days with the acid removed daily, and 0·40 grm. in 28 days when the acid was not removed. D. F. McFarland and O. E. Harder observed with $N\text{-}H_2SO_4$ a loss of 19·40 mgrms. per sq. in. per week ; and W. Rohn found with 10 per cent. sulphuric acid the losses in grms. per sq. cm. with unannealed and annealed nickel were 0·04 and 0·01 respectively during 24 hrs.' action in the cold ; 0·04 and 0·02 respectively

during one hour's action with the hot acid, and 0·08 and 0·10 respectively during 24 hrs.' action of the hot acid. R. Krulla's observations are summarized in Fig. 89. The subject was studied by B. Bogitch, and M. Straumanis. R. Irmann found that 63 per cent. sulphuric acid has the maximum action on nickel at the temp. of the water-bath; the rate of attack at 95° when the corrosion is represented by the loss in mgrms. per sq. cm., is:

Time	2	4	8	20·5	25 hrs.
Loss in weight . .	8·5	14·5	25·0	44·0	50·5

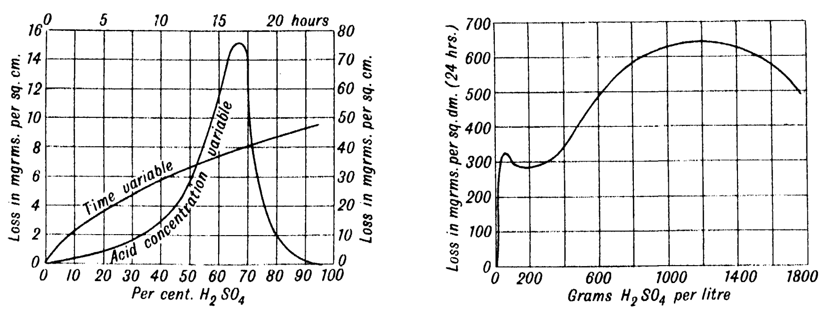
The results are plotted in Fig. 89, time variable, and using ordinates on the right. The attack by $10N$-H_2SO_4, or 38 per cent. sulphuric acid, was found to be 3 mgrms. per sq. cm. in 4 hrs.; and the attack by sulphuric acid of different concentrations, at 95°, attains a maximum with 65 per cent. sulphuric acid. The results during 4 hrs.' action, at 95°, are:

H_2SO_4 .	10·19	20·26	30·48	40·35	50·11	63·43	70·00	80·24 per cent.
Loss .	0·90	1·00	1·81	2·14	6·13	14·65	12·36	2·04

The results are plotted in Fig. 90, variable concentrations, using the ordinates on the left. Observations were made by L. Davies and L. Wright. G. C. Fink and C. M. Decroly also measured the rate of attack on nickel by sulphuric acid of different concentrations, grams H_2SO_4 per litre:

H_2SO_4 .	3·35	24·75	53·0	106·50	197·90	395·90	1322	1768 per cent.
Loss . .	62·5	122	173	152	135	168	323	248

The results are plotted in Fig. 90. O. B. J. Frazer and co-workers found that the maximum in the H˙-ion concentration curve is above the maximum for the rate



FIGS. 89 and 90.—The Action of Sulphuric Acid on Nickel.

of corrosion in sulphuric acid of different concentrations. P. B. Ganguly and B. C. Banerji studied the effect of surface tension; and N. Kameyama and K. Takahashi, the dissolution of nickel in the acid under the influence of an alternating current. R. H. Adie observed that with hot sulphuric acid, sulphur dioxide appears at 145°, but no hydrogen sulphide was observed. According to G. J. Burch and J. W. Dodgson, nickel scarcely evolves any gas with sulphuric acid of sp. gr. 1·84, but in contact with sodium, the nickel acquires a brownish film, and a few bubbles arise from the sodium.

A. Coppadoro observed that with 4 to 40 per cent. sulphuric acid, and electrolysis with an alternating current, at room temp., and a current density exceeding 50 amp. per sq. dm., nickel dissolves almost quantitatively with a 95 per cent. current efficiency; with lower current densities, the condition of the surface of the electrode has a marked influence on the amount of metal dissolved. Without electrolysis, the amount of metal dissolved by the conc. acid is imperceptible. With 50 to 60 per cent. sulphuric acid, the yield of dissolved nickel first increases to a maximum with an increase of current density, and subsequently diminishes considerably owing to the passivity of the metal. At the same time, oxygen appears along with the hydrogen. The amount of metal dissolved is increased up to 100 per cent. by the presence in the electrolyte of oxidizing agents like

potassium permanganate or hydrogen dioxide, or even by passing air through the electrolyte under conditions where the solubility without the electrolysis is scarcely affected by these agents.

A. P. Rollet observed that nickel dissolved in sulphuric acid under the influence of an alternating current of 50 cycles, and the amount of hydrogen evolved corresponded with the weight of nickel dissolved ; it increased with the speed of stirring, and with the temp. from 0° to 30°, above 30° it decreased progressively, becoming at 65° to 70° less than it was at 0°. For feeble current densities, the yield of hydrogen fell rapidly with the conc. of the acid, and then became constant ; and for stronger current densities, it rose slowly, and became constant only when the acid was very concentrated. The yield increased with the current density between 0·7 and 1·5 amp. per sq. cm., and only hydrogen was evolved ; with a higher current density, it decreased quickly, and both hydrogen and oxygen were liberated.

C. G. Fink and C. M. Decroly examined the effect with sulphuric acid in the presence of potassium chlorate, or chromic acid. N. A. Isgarischeff and S. A. Schapiro observed that the velocity of dissolution of nickel in sulphuric acid is enhanced by various chlorides in the following order : $NH_4Cl<NaCl<LiCl<KCl<MgCl_2<FeCl_2<ZnCl_2<AlCl_3<CuCl_2<FeCl_3$, whilst the activating effect of various salts is in the order $K_2SO_4<H_2SO_4<KBr<KF<KCl<KI<KNO_3<KClO_3<KIO_3<KBrO_3$. The latter series differs from that found for the dissolution of aluminium only in the order in which halogen ions are arranged. E. Salkowsky observed that the attack by dil. sulphuric acid is favoured by the presence of hydrogen dioxide. A. Sieverts and P. Lueg discussed the retarding effects of α-naphthaquinoline ; N. Isgarischeff and S. A. Schapiro, the retarding action of various salts. R. Irmann studied the effect of alloying nickel with various elements on its corrosive effects of sulphuric acid. The presence of tungsten, for instance, lessens the attack—*vide infra*, the various nickel alloys.

E. Beutel and A. Kutzelnegg observed that when nickel is dipped in a boiling soln. of **sodium thiosulphate** and lead acetate, it acquires a sequence of colours owing to the formation of lead thiosulphate and sulphide along with some free sulphur. J. I. Crabtree and G. E. Matthews observed that soln. of sodium thiosulphate in a hypo-fixing bath attacks nickel only very slightly. M. G. Levi and co-workers found that nickel dissolves very slowly, without an evolution of gas, in soln. of **potassium and ammonium persulphates.** J. W. Turrentine emphasized the analogy between the solubility of nickel in soln. of ammonium persulphate, and its solubility in soln. of **ammonium sulphate,** assisted by electrolysis.

H. Fonzes-Diacon, A. Orlowsky, and G. Little observed that when nickel is heated a little, it unites with **selenium** with incandescence ; and C. Fabre, that nickel unites with the vapour of **tellurium,** forming a telluride. A. Simek studied the action of **tellurium dioxide ;** and E. B. Hutchins, the attack by hot, conc. **telluric acid.**

According to A. Sieverts,[6] **nitrogen** does not react with nickel at temp. up to 1000°, and that the vol. of nitrogen occluded at

	15·5°	200°	400°	600°	800°	1000°
Nitrogen .	8·45	11·74	13·06	13·84	14·32	14·74 c.c.

W. Frankenburger and co-workers, and V. Lombard studied the absorption of nitrogen by highly dispersed nickel ; L. R. Ingersoll, by spluttered nickel ; and E. Rupp, the effect of absorbed nitrogen on the space-lattice. F. Wolfers observed that in the presence of nitrogen free from oxygen, nickel begins to form a volatile nitride at 300°, and that the nitride becomes unstable at 600°. This nitride also readily attacks platinum. L. R. Ingersoll said that a nitride is formed when nickel is spluttered in nitrogen, and G. Tammann studied the rate of formation of the nitride. L. R. Ingersoll and J. D. Hanawalt said that nickel does not show a critical temp. when it is cooled in the presence of nitrogen, and that no adsorption occurs. N. A. Dew and H. S. Taylor also observed that no perceptible amount of

nitrogen is absorbed by nickel between 0° and 444·6°—*vide supra*, hydrogen. Observations were made by J. C. Stimson, O. Schmidt, J. Hagenacker, C. Laffitte and P. Grandadam, and H. N. Warren. G. Tammann detected no chemical action at 700°. B. Jones studied the hardening of nickel by nitridization; E. Rupp, the optical properties of the adsorbed film; G. I. Finch and J. C. Stimson, the electrical properties of the metal when adsorbing nitrogen; T. Skutta, the effect of adsorbed nitrogen on the electrical resistance of the metal; and G. B. Kistiakowsky, the ionization potential of the metal charged with nitrogen. O. Meyer found that nickel is slightly attacked by **titanium nitride** at 1600°. P. Neogi and B. B. Adhicary observed that no chemical union occurs when a mixture of hydrogen and purified nitrogen is passed over reduced nickel. L. R. Ingersoll observed that a film of nickel spluttered in nitrogen, and afterwards heated in hydrogen, furnishes ammonia—10 to 20 mgrms. with a film of 200 sq. cm. E. Keunecke used a nickel molybdenum catalyst in the synthesis of ammonia from hydrogen and nitrogen.

F. Vorster observed that heated nickel decomposes **ammonia** gas into its elements, and P. A. Guye and F. Schneider added that some decomposition occurs when the temp. exceeds 300°. The reaction was studied by C. H. Kunsman, J. S. Vanick, P. Grandadam, and G. T. Beilly and G. C. Henderson. G. Gore found that nickel is insoluble in liquid ammonia. W. A. Dew and H. S. Taylor observed that 1 grm. of nickel at

	0°	110°	218°	305°
NH_3 adsorbed . . .	0·875	0·457	0·100	0·065 c.c.

O. Schmidt, and N. I. Nikitin and W. I. Scharkoff studied the subject. U. R. Evans observed very little action when nickel is exposed over water saturated with ammonia, although some specimens were darkened considerably. W. Guertler and T. Liepus found that nickel is attacked by 10, 50, and 70 per cent. aq. ammonia during 8 days' exposure; D. F. McFarland and O. E. Harder observed that N-NH_4OH dissolved 15·90 mgrms. per sq. in. per week; and A. J. Hale and H. S. Foster could detect no loss with nickel in contact with 0·2N-NH_4OH for 28 days. T. H. Chilton and W. R. Huey found that the action of ammonia gas at low temp. is small, but great at a high temp. in presence of oxygen. For the nickel catalyst in the synthesis of ammonia, *vide infra*. E. Keunecke studied the nickel-molybdenum catalyst in the synthesis of ammonia from nitrogen and hydrogen. C. Matignon and G. Desplante noted the oxidation of nickel when exposed to air in the presence of ammonia. W. R. E. Hodgkinson and co-workers found that fused **ammonium nitrate** dissolves nickel, giving off ammonia and a little hydrogen; and E. Divers, that the metal is insoluble in an ammoniacal soln. of ammonium nitrate. H. Ehrig, and F. W. Bergstrom studied the solubility of the metal in a soln. of ammonium nitrate. K. A. Hofmann and co-workers gave for the relative rates of attack by the vapour of **ammonium chloride** at 250° to 350°: Fe>Cu>Ni>Ag>Hg. P. Junius also studied the action of the vapour on nickel. A. W. Browne and co-workers observed the attack of nickel by **ammonium azide.**

P. A. Guye and F. Schneider observed that when a mixture of **nitrous oxide** and hydrogen is passed over heated nickel, 3 to 7 per cent. of the oxide is reduced to ammonia. E. Schröder and G. Tammann studied the rate of attack; H. W. Melville compared the effects with the two isotopes of hydrogen; and J. A. Hedvall and E. Gustavson, the null effect of a magnetic field. According to P. Sabatier and J. B. Senderens, when finely-divided nickel is heated in **nitric oxide,** nitrogen and nickel oxide are produced. The reaction was studied by G. Tammann and W. Köster. M. Centnerszwer and H. Zyskowicz observed no action on metal foil at 50° to 150°, but nickel powder is attacked, and at 280° to 290° the blue monoxide is formed. R. S. Felgate said that the decomposition occurs only if the finely-divided nickel be suspended in hot water, but colloidal soln. of nickel, prepared by

spluttering nickel cathodes under water, does not act in the same manner. E. Schröder and G. Tammann measured the rate of attack of nickel by nitric oxide. According to J. K. Dixon and W. Steiner, N. D. Zelinsky and M. B. Turowa-Pollak, P. Sabatier and J. B. Senderens, and P. Neogi and B. B. Adhicary, when a mixture of nitric oxide and hydrogen is passed over reduced nickel, ammonia is formed, but the reaction is not quantitative—it begins at 300°, but once it is in progress, the temp. may be lowered to 120°. Nitric oxide alone, when passed over reduced nickel, does not yield nitride, nitrite, or nitrate. P. A. Guye and F. Schneider observed that both ammonia: $2NO+5H_2=2NH_3+2H_2O$, and nitrogen: $2NO+2H_2=N_2+2H_2O$, are simultaneously formed when a mixture of nitric oxide and hydrogen is passed over nickel. The relative properties depend on the nature of the catalyst, and on other conditions. There is an optimum concentration of hydrogen yielding the highest proportion of ammonia. Under favourable conditions, 70 per cent. of the nitric oxide may yield ammonia. The most favourable temp. is 250° to 300° ; below this range, the reduction takes place slowly, and above this range, the nickel becomes less active, and some ammonia is dissociated with hydrogen and nitrogen. P. A. Guye and F. Schneider found that when a mixture of hydrogen and **nitrogen peroxide** is passed over heated nickel, 25 to 39 per cent. of the peroxide may be converted into ammonia. P. Sabatier and J. B. Senderens said that nitro-nickel, Ni_2NO_2, analogous with nitro-cobalt, is formed by the action of nitrogen peroxide on nickel, but the work of J. R. Park and J. R. Partington makes it doubtful if a chemical individual is really produced. J. J. Sudborough found that **nitrosyl chloride** attacks nickel very slowly at 0° to 100° during a few days' exposure.

Nickel is oxidized by **nitric acid,** forming nitrogen and nitric oxide gases, and a soln. of nickelous nitrate. According to J. J. Ackworth and H. E. Armstrong, the metal is slowly attacked by nitric acid (1 : 2), and the gas evolved—about 33 c.c. per gram at 13°—contains about 4·3 per cent. of nitric oxide, 85·10 per cent. of nitrous oxide, and 10·36 per cent. of nitrogen. It was also found that 6·17 c.c. of hydrogen were given off per gram of nickel—probably the hydrogen was originally occluded in the metal, and was not oxidized by the acid. C. Montemartini reported that the dissolution of a gram of nickel in an excess of 27·5 per cent. nitric acid furnishes 0·01874 grm. of ammonia, 0·00060 grm. of nitrous acid, 0·00749 grm. of nitrous oxide, and 0·00071 grm. of nitrogen—total, 0·02754 grm. The nitric oxide which is evolved is of secondary origin, being derived from the decomposition of the nitrous acid. No hydroxylamine was detected amongst the products of the reaction. R. Irmann found that the rate of attack by $10N$-HNO_3, or 48 per cent. nitric acid, is 1200 mgrms. of nickel per sq. cm. per hour; J. I. Crabtree and G. E. Matthews, that with 5 per cent. nitric acid, there is a loss of 3·1 grms. per 100 sq. cm. per day; W. Guertler and T. Liepus, that the metal is attacked by 50 per cent. nitric acid, and by hot or cold 10 per cent. nitric acid within 8 hrs.; A. J. Hale and H. S. Foster, that the losses in weight by polished nickel at 17° to 20° in 500 c.c. of $0{\cdot}2N$-HNO_3, are 4·2 grms. per sq. dm. in 7 days with the acid daily renewed, and 2·1 grms. per sq. dm. in 28 days when the acid is not renewed; D. F. McFarland and O. E. Harder, that nickel in contact with N-HNO_3 lost 2270·0 mgrms. per sq. in. per week; and W. Rohn, that with unannealed and annealed nickel, and 10 per cent. nitric acid, the losses were, respectively, 0·65 and 0·50 grm. per sq. dm. in 24 hrs. with cold acid, and, respectively, 3·7 and 9·07 grms. per sq. dm. per hour with hot acid. R. Krulla's observations are summarized in Fig. 88. The action of nitric acid on nickel was also studied by B. Bogitch, and C. C. Palit and N. R. Dhar. A. Sieverts and P. Lueg studied the retardation by naphthaquinoline. A. Quartaroli observed that the presence of urea slows down the action of nitric acid; and B. C. Banerji and N. R. Dhar, that with 40 per cent. nitric acid, the reaction was accelerated by the presence of ferrous sulphate, ferric chloride, and nickel nitrate, but it was retarded by ferric nitrate. According to W. W. Hollis, if 98 per cent. nickel be in contact with fuming nitric

acid, a greyish-white magnetic powder is formed. H. St. Deville, and J. Nicklès observed that nickel may become passive in conc. nitric acid, provided, added W. W. Hollis, the temp. be below 80°—*vide supra*. A. Coppadoro found that on electrolyzing 10 per cent. nitric acid with an alternating current, the metal readily dissolved, but with a soln. of **sodium nitrate,** and an alternating current, the metal became passive—no nickel dissolved, and no gas was evolved. G. R. White studied the electrolytic corrosion of nickel as anode in soln. of sodium nitrate. W. R. E. Hodgkinson and A. H. Coote found that nickel is vigorously attacked by molten **potassium nitrate.** W. Guertler and T. Liepus observed that nickel is attacked within 8 hrs. by **aqua regia,** and the reaction was studied by C. F. Bonilla.

B. Pelletier observed that nickel is attacked by the vapour of **phosphorus ;** and N. Konstantinoff also found that molten phosphorus furnishes phosphides ; but H. E. Patten observed no reaction at ordinary temp. J. Garnier recommended phosphorus as a deoxidizer for nickel on the assumption that the non-malleability of the metal is due to oxygen. He said that 0·3 per cent. of phosphorus is sufficient to render the nickel soft and malleable, a greater quantity of phosphorus makes the metal harder and less malleable. The phosphorus is added in the form of phosphide of nickel, containing about 6 per cent. of phosphorus. Nickel containing 0·25 per cent. of phosphorus may easily be rolled into leaves 0·5 mm. thick. H. L. Haken, and A. Granger found that **phosphorus trichloride** attacks heated nickel, forming phosphides. According to P. Neogi and B. B. Adhicary, phosphine is formed when hydrogen is passed over a mixture of nickel and **phosphorus pentoxide** at a dull red-heat. R. Tupputi found that dil. **phosphoric acid** very slowly dissolves nickel with the evolution of hydrogen, and the formation of nickel phosphate. W. Rohn observed that unannealed and annealed nickel with 10 per cent. soln. of phosphoric acid lost, respectively, 0·004 and 0·004 grm. per sq. dm. in 24 hrs. in the cold, and respectively, 0·036 and 0·004 grm. per sq. dm. per hour when the acid was hot. P. R. Kosting and C. Heins found that the penetration of nickel by the corrosive action of 85 per cent. phosphoric acid is equivalent to 370×10^{-5} cm. per day. The reaction was studied by A. M. Portevin and A. Sanfourche. P. Breteau found that nickel powder decomposes water in the presence of **sodium hypophosphite :** $NaH_2PO_2+H_2O=H_2+NaH_2PO_3$, followed by : $NaH_2PO_3+H_2O=NaH_2PO_4+H_2$.

A. F. Gehlen observed that when nickel and **arsenic** are heated together, union occurs without incandescence ; and the subject was studied by F. Ducelliez, and K. Friedrich and F. Bennigson. H. E. Patten found that nickel is slightly corroded by **arsenic trichloride ;** and A. Granger, that an arsenide is formed when nickel is exposed to the vapour of arsenic trichloride. G. Arrivaut represented the reaction by $6Ni+2AsCl_3=3NiCl_2+Ni_3As_2$. L. Kahlenberg and J. V. Steinle observed a slight plating of nickel immersed in arsenic trichloride at room temp., and a slight reaction at 100°. T. Bergman, F. Stromeyer, W. Guertler, and F. Roessler found that nickel unites with **antimony** when the two elements are melted together ; and the subject was studied by F. Ducelliez. G. Hägg and G. Funke studied the alloys with **bismuth.** According to E. Vigouroux, nickel antimonide is formed when the vapour of **antimony trichloride** acts on heated nickel ; and H. E. Patten found that nickel is not corroded by **antimony pentachloride.** P. Lebeau found that **copper arsenide,** and **copper antimonide** readily give up arsenic or antimony to nickel. G. Hägg and G. Funke, G. Voss, and A. M. Portevin studied the compounds of nickel and **bismuth** ; and H. Giebelhausen, the compounds with **vanadium.** F. E. Brown and J. E. Snyder found that **vanadium oxytrichloride** has no action on nickel.

J. W. Döbereiner,[7] R. Tupputi, O. L. Erdmann, O. Ruff, O. Ruff and W. Martin, W. Ross, L. Guillet, R. Irving, and J. B. J. D. Boussingault observed that molten nickel readily takes up **carbon,** rendering the metal brittle ; the effect on the m.p. has been examined by K. Friedrich and A. Leroux, H. McK. Elsey, O. Meyer, O. Ruff and co-workers, N. B. Pilling and T. E. Kihlgren, and E. Briner and

R. Senglet. **Nickel tritacarbide,** Ni_3C, is formed analogous to cementite, Fe_3C—*vide* **5.** 39, 20. The carbides were studied by W. E. Gard, G. Meyer and F. E. C. Scheffer, and F. Fischer and H. Bahr; the cementation of nickel by carbon, by J. B. J. D. Boussingault; and the diffusion of carbon in the metal, by G. Tammann and K. Schönert, who also gave $-9·2$ Cals. for the heat of formation of nickel tritacarbide. J. Schmidt did not obtain any other carbide. D. H. Browne and J. F. Thompson said that nickel, like iron, takes up carbon by cementation, and they found that after 10 hrs.' heating between 700° and 900°, malleable and electrolytic nickel take up carbon so that before cementation the carbon contents were, respectively, 0·15 and 0·18 per cent.; and after cementation, respectively, 0·33 and 0·43 per cent. Nickel in a cupola furnace absorbs almost as much carbon as pig-iron does, so that pig-nickel may contain 2 to 3 per cent. of carbon. H. McK. Elsey carbonized the metal by heating in nitrogen and a hydrocarbon gas. According to O. Ruff and W. Martin, the solubility of carbon in nickel reaches a maximum of 6·42 per cent. at 2100°. Carbon adds strength and hardness to all grades of malleable nickel; it makes the metal work better whilst hot, but it increases the difficulty of working the metal cold. When fully annealed, high-carbon nickel is harder than low-carbon nickel, and it hardens faster under cold-working. With about 0·40 per cent. of carbon, the carbon begins to separate, and the separation is accompanied by a loss of malleability. The presence of graphitic carbon is harmful. T. Mishima studied the carbon brittleness of nickel and of its alloys. O. Ruff and W. Martin represented the effect of carbon on hot-rolled nickel rods as follows—when the term "normal" refers to rods as rolled, without annealing:

Carbon Per cent.	Hardness Brinell's		Elongation Per cent.		Yield Point lbs. per sq. in.		Tensile Strength lbs. per sq. in.	
	Normal	Annealed	Normal	Annealed	Normal	Annealed	Normal	Annealed
0·063	107	89	37·1	44·5	21,375	23,500	68,875	67,500
0·09	109	92	44·2	46·0	23,750	22,000	73,125	70,000
0·26	135	99	37·6	42·0	34,375	29,625	93,625	87,000

C. Sandonnini observed that nickel had no effect as a catalyst on the hydrogenation of carbon: $C+2H_2=CH_4$. O. Meyer found that nickel at 1600° is appreciably attacked by the **metal carbides**—silicon, molybdenum, and chromium.

According to I. L. Bell, and G. Charpy, when nickel is heated in **carbon monoxide,** a little carbon may be separated; but the metal suffers no perceptible change. H. A. and T. Bahr studied the reaction $2CO \rightleftharpoons C+CO_2$ in the presence of nickel, and found that between 270° and 420° some nickel carbide is formed. C. J. Smithells observed that nickel, under ordinary conditions, contains occluded carbon monoxide. E. Bergner, H. S. Taylor and R. M. Burns, J. C. Stimson, N. I. Nikitin, and A. Villachon and G. Chaudron studied the absorption of carbon monoxide by nickel; and G. I. Finch and J. C. Stimson, the electric charge of the metal when adsorbing carbon monoxide. L. Mond and co-workers observed that when nickel is heated below 100° in a current of carbon monoxide, a volatile carbonyl is formed—*vide* **5.** 39, 27—and, according to N. Hudson, this also occurs with the nickel in nickel-steel. G. Meyer and F. E. C. Scheffer obtained a carbide at 270°, and V. Kohlschütter and A. Nägeli found that carbon is deposited at 500°. If finely-divided nickel be heated over 350° in carbon monoxide, carbon and carbon dioxide are formed. J. Garnier stated that the luminosity of the flame of carbon monoxide, in the manufacture of iron and steel, and the separation of nickel and nickel oxide in the flues of a furnace in which ferro-nickel is heated, is due to the formation of volatile compounds of iron and nickel with carbon monoxide. F. Zimmermann showed that in the blast-furnace treatment, nickel breaks up carbon monoxide: $2CO=C+CO_2$. The reaction was studied by S. Horiba and T. Ri. W. A. Bone and G. W. Andrew, C. M. Loane, H. A. and T. Bahr, and R. Schenck and H. Wesselkock studied the effect of nickel and of metal oxides on the oxidation of carbon monoxide; H. A. and T. Bahr observed that some nickel

carbide is formed. J. E. Nyrop, W. E. Gibbs and H. Liander, K. Fujimura and S. Tsuneoka, K. Chakravarty and J. C. Ghosh, H. S. Elworthy and S. Williamson, and E. F. Armstrong and T. P. Hilditch showed that in the presence of heated nickel, carbon monoxide is reduced by hydrogen to form methane: $CO+3H_2=CH_4+H_2O$. P. Sabatier and J. B. Senderens observed that the reduction occurs at about 250°. The reaction, with zinc as catalyst, proceeds $CO+2H_2=CH_3OH$; and with copper as catalyst, $CO+H_2=CH_2O$. If a mixture of water vapour and carbon monoxide is heated between 500° and 1000°, in the presence of nickel as a catalyst, L. Vignon, and S. Kodama observed that methane is produced. K. Fujimura and co-workers studied the action of hydrogen sulphide and carbon disulphide in the action of nickel as a catalyst on the hydrogenation of carbon monoxide. H. W. Melville compared the effect with the two isotopes of hydrogen. G. Fester and M. Schwazappa investigated the electrocatalytic reduction of carbon monoxide; and M. Hansen studied the action of producer gas.

I. L. Bell found that a current of **carbon dioxide** passed over spongy nickel at a dull red-heat furnishes some carbon monoxide. R. Schenck and H. Wesselkock studied the action of the oxides of calcium, magnesium, manganese, and aluminium on the oxidation of nickel at 900° in an atm. of carbon dioxide, and they observed that no carbon monoxide is formed at 600°, and less than 1 per cent. at 900°; but if magnesia, or manganese oxide, be present, 40 per cent. of carbon monoxide is formed at 600°. Lime promotes the reaction slightly. N. I. Nikitin, and H. S. Taylor and R. M. Burns studied the adsorption of carbon dioxide by nickel; and G. I. Finch and J. C. Stimson, the electrical charge of the metal when adsorbing the gas. H. Koch and H. Küster studied the catalytic reduction of the dioxide with hydrogen. W. W. Russell and H. S. Taylor observed the promotor action of thoria when nickel is the catalyst in the hydrogenization of carbon dioxide; $CO_2+4H_2=CH_4+2H_2O$. T. Bergman observed that the metal is attacked by a soln. of carbonic acid. W. Guertler and T. Liepus found that nickel is attacked by carbon dioxide and air during 8 hrs.' exposure; and R. Robl studied the solubility of nickel in water containing carbon dioxide in soln. E. Müller and A. Luber represented the solubility of nickel, in mgrms. per litre, at 20° and 100°, in water saturated with carbon dioxide under a press. of 50 atm., at different temp., by Fig. 91.

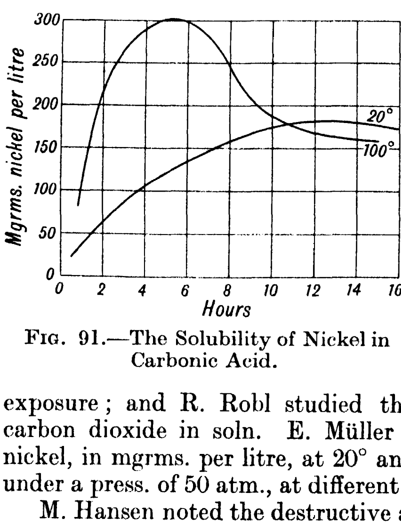


FIG. 91.—The Solubility of Nickel in Carbonic Acid.

M. Hansen noted the destructive action of **producer gas** on nickel. H. Hollings and R. H. Griffith studied the adsorption of **hydrocarbons** by the metal; and G. Charlot, their catalytic oxidation. W. Ramsay studied the effect of nickel on the formation of **petroleum**; J. C. Elgin and co-workers, on **sulphur-naphtha,** and **sulphur-petroleum**; and E. W. Kanning and O. W. Brown, the decomposition of **kerosene.** B. Yamaguti studied the thermal decomposition of **methane,** with nickel as catalyst; and W. E. Gard observed that the metal increases in weight when it is heated in a current of methane; and he added that no carbon is taken up so that the increase in weight was attributed to the association of nickel with the metal. The subject was studied by R. C. Cantello. K. Yoshikaka observed that with a nickel catalyst, methane is oxidized quantitatively by air or oxygen in accord with: $2CH_4+O_2=2CO+4H_2$—a reaction studied by W. P. Yant and C. O. Hawk, H. Fujimoto, and I. E. Adaduroff. N. A. Klyukvin and S. S. Klyukvina studied the oxidation of methane by carbon dioxide, and by steam. R. Klar, E. G. Insley, and B. Foresti studied the adsorption of **ethane** by nickel; and R. C. Cantello, the thermal decomposition of ethane in presence of nickel.

W. A. Lazier and H. Adkins found that 100 grms. of nickel, reduced by hydrogen, adsorbed 84 c.c. of **ethylene** at normal temp. and press., and nickel, reduced by alcohol, adsorbed 61 c.c. of that gas. The adsorption of ethylene by nickel was studied by H. S. Taylor and R. M. Burns, E. W. R. Steacie and H. V. Stovel, R. Klar, J. Eckell, O. Schmidt, W. A. Lazier and H. Adkins, E. G. Insley, G. M. Schwab, K. Ablezowa and S. Robinsky, and B. Foresti; and the reduction and polymerization of ethylene by nickel at 400°, by H. W. Walker, F. Thorén, and R. C. Cantello. P. Sabatier and J. B. Senderens observed that with nickel as a catalyst, ethylene is reduced to ethane, and the reaction was discussed by H. Adkins and L. W. Covert, W. D. Bancroft and A. B. George, L. W. Covert and co-workers, H. Dohse and co-workers, J. Eckell, A. W. Gauger, F. Fischer and K. Meyer, B. Foresti, F. E. Frey and D. F. Smith, W. E. Gibbs and H. Liander, J. Horiuti and M. Polanyi, A. Kailan and co-workers, J. N. Pearce and co-workers, R. N. Pease and L. Stewart, R. Klar, H. zur Strassen, E. K. Rideal, O. Schmidt, H. W. Underwood, and K. Yoshikawa. M. Trauber studied the voltaic potential of the metal during the hydrogenation of ethylene. In a similar manner P. Sabatier and J. B. Senderens, and F. E. Frey and D. F. Smith hydrogenized **propylene** to propane, **trimethylethylene** to methylbutane, **hexene** to hexane, **octene** to octane. Similar reactions with other unsaturated hydrocarbons were studied by L. Clarke and W. N. Jones, C. J. Enklaar, A. Korczynsky and co-workers, M. Murat and G. Amouroux, and P. Sabatier and M. Murat. J. H. Long and co-workers, B. Kubota and K. Yoshikawa, F. Thorén, R. Truffault, and N. D. Zelinsky and M. B. Turowa-Pollak studied the hydrogenation of **benzene** to hexamethylene, and the dehydrogenation of **hexamethylene** with nickel as catalyst, a subject discussed by W. D. Bancroft and A. B. George, and H. Adkins and co-workers. F. H. Rhodes and co-workers studied the corrosion of nickel by **phenols.** J. K. and S. C. Chowdhury studied the effect of nickel as catalyst on the oxidation of **toluene.** H. Moissan and C. Moureu found that reduced nickel favoured the thermal decomposition of **acetylene,** which occurs with incandescence, yielding carbon and hydrocarbons; and K. Fukagawa studied the polymerization of acetylene. P. Sabatier and J. B. Senderens observed that acetylene can be hydrogenized to ethane; and A. Müller and A. Sauerwald, that **aluminium triethyl** is not affected by nickel black. H. W. Melville compared the effects with the two isotopes of hydrogen. A. A. Balandin and A. M. Rubinstein studied the dehydrogenation of cyclic hydrocarbons.

P. Sabatier and J. B. Senderens, R. Douris, G. Darzens, A. Skita, E. H. Boomer and H. E. Morris, F. Bodroux and F. Taboury, and H. Adkins and L. W. Covert reduced aldehydes and ketones to the corresponding alcohols. Numerous other hydrogenations of a like nature have been reported. Thus, G. Darzens converted acetophenone to butylbenzene, and phenylbutanone to butylbenzene; E. J. Lush reduced naphthalene; A. Brochet, phenol; A. Mailhe and F. de Godon, the aromatic ketones—*e.g.*, acetophenone, phenylethylketone, phenylbutylketone, phenylpropylketone, phenyl*iso*propylketone, benzyl*iso*propylketone, benzophenone, phenylbenzylketone, and *p*-tolylbenzylketone—to the corresponding hydrocarbons, and benzoyl chloride, at 270° to 280°, to benzene, toluene, and diphenyl. H. van Beresteyn observed that heptyl alcohol furnishes *n*-hexylene and methyl alcohol. P. Sabatier and J. B. Senderens found that nitromethane becomes methylamine; nitroethane becomes ethylamine mixed with some diethylamine, triethylamine, and ammonia; nitrobenzene, also studied by L. Reichardt, becomes aniline; and analogous reductions occur with nitrotoluene, and nitronaphthalene. C. Mignonac observed that an analogous reduction occurs with dinitrobenzene, dinitrotoluene, and nitrophenols. The reduction of the nitrous esters—*e.g.*, methyl, ethyl, propyl, butyl, and amyl nitrites—was studied by G. Gaudion. P. Sabatier and J. B. Senderens observed that the oximes are reduced by hydrogen in the presence of the nickel catalyst, thus, acetoxime furnishes primary and secondary amines with a little tertiary amine; ethanoxime yields mainly diethylamine; and oenanthaloxime, mainly a primary amine. These reactions were also studied by J. Aloy and V. Brustier, G. Amouroux, H. L. Bender, A. Borchers, T. S. Carswell, F. F. Diwoky and H. Adkins, W. E. Garner and D. N. Jackman, M. Godchot, M. N. Goswami, R. Hocart, V. Ipatéeff, I. L. Karczag, A. Korczynsky, A. Mailhe and co-workers, W. Meigen and G. Bartels, A. E. Mitchell and A. L. Marshall, R. N. Pease and H. S. Taylor, H. Plauson and J. A. Vielle, C. Schuster, H. S. Taylor and co-workers, K. Yoshikawa, K. S. Ablezova and S. Z. Roginsky, and E. Tiede and W. Jenisch.

Numerous other studies on the hydrogenation of organic compounds in the presence of the nickel catalyst, or on the thermal decomposition of organic compounds in the presence of this catalyst, have been made. For example, M. Gaverdovskaja studied the dehydrogenation of hydrocarbons; H. Adkins and co-workers hydrogenated ethyl acetoacetate, dihydracetic acid, and phenol, at 27 to 350 atm. press.; G. M. Schwab and W. Brennecke investigated the hydrogenation of ethyl cinnamate; J. N. Pearce and co-workers, and W. W. Russell and R. F. Marschner, the catalytic decomposition of the esters—*e.g.*, methyl, ethyl, and propyl acetates, and methyl propionate; M. S. Ebert, and M. E. Kinsey and H. Adkins, acetaldehyde; C. F. Winaus and H. Adkins, the alkylation of the amines; S. Komatsu and C. Tanaka, aniline; T. Bersin, the dehydrogenation of mercapto-compounds; A. A. Balandin, the dehydration of *cyclo*hexane; A. A. Balandin and A. M. Rubinstein, cyclic hydrocarbons; F. Fischer and K. Meyer, benzene; S. J. Green, aromatic nitro-compounds; V. Grignard, methylheptenols; A. Korczynsky and co-workers, the hydrogenation of aromatic hydrocarbon halides; J. von Braun and co-workers, anthraquinone, phenanthraquinone, benzanthraquinone, acenaphthenequinone, acenaphthalene, aldehydes, carbazoles, nitriles, quinolines, indoles, indenes, 2 : 2′-dihydroxydiphenyl, phenetidine, and xanthone; A. Feldmann, aromatic compounds; K. Negoshi, acetaldehyde; S. Komatsu and T. Yukitomo, *l*-menthol; S. Komatsu and C. Tanaka, *cyclo*hexylamine; S. Komatsu and B. Masumoto, *cyclo*hexanol; A. Brochet and co-workers, phenols, naphthols, octene, cinnamic acid, piperonylacrylic acid, onethole, eugenol, safrole, and nitro-, azoxy-, and hydrazo-derivatives; G. M. Schwab and W. Brennecke, cinnamic esters; H. van Beresteyn, heptyl alcohol; P. Sabatier and G. Gaudion, pinene, limonene, camphene, menthene, *cyclo*hexene, *cyclo*hexanol, pulegone, eucalyptol, terpene, and terpineol; M. Tanaka, unsaturated compounds like azoxybenzene and ricinostearine; and C. Kelber, diphenyldiacetylene, and azolbenzene.

A. Kailan and O. Stüber, and T. Jurgens and W. Meigen found that the hydroxyl groups of the hydroxy-fatty acids, like oleic acid, and ricinoleic acid, are readily hydrogenated at about 200°. P. Sabatier and J. B. Senderens discussed the use of the nickel catalyst in the commercial hardening of unsaturated fats and oils—*e.g.*, linseed oil, and cotton-seed oil—by reducing or hydrogenating them at about 250°. The hardened oils form hard fats suitable for the manufacture of soap and candles, and in some cases solid, edible fats. This subject was discussed by P. Sabatier, *La catalyse en chimie organique* (Paris, 1913); C. Ellis, *The hydrogenation of Oils* (New York, 1914); G. Hefter, *Technologie der Fette und Oele* (Berlin, **3.** 795, 994, 1910); and L. Ubbelohde and F. Goldschmidt, *Handbuch der Chemie und Technologie der Oele und Fette* (Leipzig, **3.** 152, 1910).

The subject was discussed by O. G. Bennett and C. B. Jackson, J. Leimdörfer, A. Kailan and J. Kohberger, W. W. Myddleton, L. R. Williams and C. A. Jacobson, E. J. Lush, H. T. Offerdahl, T. W. A. Shaw, S. Ueno, G. Riess, F. Bordas, A. S. Koss, S. Jozsa, H. L. Barnitz, H. Kahlenberg and G. J. Ritter, G. Meyerheim, E. Erdmann, and F. Fischer and K. Peters. M. Tanaka discussed the hydrogenation of perilla oil, hemp-seed oil, chrysalis oil, and shark oil; G. Kita and co-workers, soja-bean oil, and herring oil; E. J. Lush, linseed oil, soja-bean oil, cotton-seed oil, and olive oil; A. S. Richardson and co-workers, cotton-seed oil, arachis oil, and soja-bean oil; M. de Roubaix, oleic acid and olein; W. Normann and W. Pungs, cotton-seed oil, olive oil, linseed oil, and sesame oil; and E. F. Armstrong and T. P. Hilditch, whale oil.

J. Formanek found that the action of **carbon tetrachloride** on nickel during 8 months was too small to affect the use of that metal as a container. F. H. Rhodes and J. T. Carty observed that nickel is not corroded by the vapour or by liquid carbon tetrachloride at room temp. The subject was studied by L. Vernitz and A. Kudinova. H. E. Patten observed no action with carbon tetrachloride, **ethyl chloride,** or with **chloroform.** J. Formanek said that **trichloroethylene,** and **tetrachloroacetylene** have too small an action on nickel during 8 months to affect the use of that metal as a container. R. Krulla's observations are summarized in Fig. 88. H. R. S. Clotworthy recommended nickel for resisting the action of **carbon disulphide.** H. Rupe and A. Heckendorn studied the hydrogenation of organic **cyanogen** compounds with nickel as catalyst; J. von Braun and co-workers, W. W. Russell and R. F. Marschner, C. H. D. Clark and B. Topley, and W. L. Faith and D. B. Keyes, the oxidation and decomposition of **alcohol;** F. H. Rhodes and co-workers, the action of **phenols;** R. Krulla's observations on

the action of **formic acid** on nickel are summarized in Fig. 88. B. B. Wescott and C. J. Engelder studied the thermal decomposition of formic acid with nickel as catalyst. W. Guertler and T. Liepus found that nickel is attacked by **acetic acid** during 8 hrs.' exposure; whilst W. Rohn showed that with unannealed and annealed nickel, 10 per cent. acetic acid dissolved, respectively, 0·000 and 0·004 grm. per sq. dm. in the cold during 24 hrs., and the hot acid dissolved, respectively, 0·012 and 0·004 grm. per sq. dm. in an hour; and M. Vuk found that the nickel lost from 0·15 to 0·65 mgrm. per 100 sq. cm. after boiling in 5 per cent. acetic acid for 2½ hrs. R. Krulla's observations are summarized in Fig. 88. E. Salkowsky observed that glacial acetic acid containing hydrogen dioxide has no perceptible action on nickel in the cold. A. Coppadoro found that the solubility of nickel in 5 per cent. acetic acid is considerably augmented when the metal is used for electrodes with an alternating current. H. F. Whittaker said that nickel resists the action of **chloroacetic acid** better than does lead; G. R. White, the electrolytic corrosion of nickel as anode in soln. of **sodium acetate**; H. L. Riley studied the corrosive action of **sodium acetate.** H. J. French said that nickel resists the vapours of **benzoic acid** at 250° better than does monel metal or copper. H. L. Riley studied the corrosive action of **sodium benzoate.** R. Krulla's observations on the corrosive action of **lactic acid,** and **tartaric acid** are summarized in Fig. 88. H. L. Riley studied the corrosive action of **sodium tartrate.** C. B. Gates said that nickel is not attacked by **oleic acid.** G. R. White, and H. L. Riley studied the electrolytic corrosion of nickel as anode in soln. of **sodium tartrate**; H. L. Riley also studied the action of **sodium citrate, oxalate, malate, phthalate,** and **salicylate.** J. N. Pearce and C. N. Ott studied the mechanism of the catalytic decomposition of esters by nickel.

J. Terwellen, and G. Tammann studied the adsorption of **methyl violet,** and **methylene blue** by nickel wires; and A. Kemper found a great reduction in the absorptive power with wires that have been heated. O. B. J. Fraser, and R. E. Wilson and W. H. Bahlke examined the effect of **oil-refining products**; B. S. Srikantau, the adsorption of **sodium linoleate** on nickel; O. Bauer and H. Arndt, the action of washing agents, **soap,** and bleaching soln.; and W. Thomson and F. Lewis, the absence of any effect on **indiarubber.** R. Krulla's observations on the effect of **carbolic acid,** and of **tannin** on nickel are summarized in Fig. 88. J. I. Crabtree and G. E. Matthews found that **hydroquinone** and **pyrogallol** photographic developing baths do not attack nickel. H. E. Searle and co-workers examined the tolerance of **wines** for nickel and other metals. T. E. Hollingshead and T. J. Otterbacher found nickel useful as a container for **vanilla** flavouring materials; and B. Lampe observed that nickel containers darken **wort.** The action of **milk** on nickel and its alloys was studied by E. C. Badeau, K. Birnbaum, C. Gerber, G. N. Quam, R. J. McKay and co-workers, H. A. Trebler and co-workers, and W. A. Wesley and co-workers—*vide infra*, physiological action; and G. N. Quam found that whilst chrome-steel suffered no perceptible loss, nickel lost the following amounts in mgrms. per sq. dm. when exposed to milk for 30 minutes:

	20°	45°	62·8°	80°	90°	95°
Loss	0·86	3·442	5·85	6·54	3·442	1·22

B. Bleyer and J. Schwaibold found that with **tea** and **coffee** at 75°, the losses suffered by nickel, in grams per sq. m. in 24 hrs., were:

Time .	10″	1′ 10″	5′ 10″	42′ 30″	2·5 hrs.	5 h. 40′	22 h. 40′
Tea .	9·2	5·8	5·0	3·7	3·7	3·2	1·1
Coffee .	4·0	2·1	1·1	0·6	0·3	—	0·2

E. Raub studied the action of leek, onion, and mustard juices on the metal. The growing use of nickel for **cooling vessels** and chemical plant has stimulated investigations into the action of liquids and food-stuffs on nickel vessels—*vide infra,* physiological action. Nickel may be dissolved or adsorbed by food-stuffs,

and the general results show that the slight contamination of food-stuffs owing to the attack on nickel cooking vessels is quite harmless, physiologically.

Observations were made by E. Cohen, H. E. Cox, M. Donauer, K. R. Drinker and co-workers, W. S. Dzierzgowsky, K. Farnsteiner and co-workers, F. Geerkens, V. G. Gheroghiu-Ploesti, P. F. von Hamel-Roos, W. T D. Hartley, T. E. Hollingshead and T. J. Otterbacher, O. F. Hunziker and co-workers, A. Johnston, B. Lampe, K. B. Lehmann, E. Ludwig, R. J. McKay and co-workers, C. L. Mantell, H. T. Offerdahl, A. M. Portevin, M. J. Prucha, A. Riche, W. van Rijn, A. Rohde, E. Schell, M. Schlotter, E. Schulze, F. B. Stevens, H. A. Trebler and co-workers, H. Vogel, M. Vuk, and W. A. Wesley and co-workers.

M. Feszczenko-Czopowsk [8] studied the cementation of nickel by **boron,** and H. Giebelhausen, and H. Moissan observed that nickel unites with boron when a mixture of the two elements is heated above 1200°—**5.** 32, 4. C. Winkler, and W. Guertler and G. Tammann made analogous observations with respect to **silicon.** According to D. H. Browne and J. F. Thompson, silicon is present in small proportions in all furnace-refined nickel, usually in amounts below 0·25 per cent. Such small amounts have very little influence on the metal, but larger proportions increase the hardness and strength, but decrease the ductility. Silicon also reduces or destroys the malleability of the metal at a red-heat—*vide* **6.** 40, 13. The subject was discussed by B. Borén, and K. Grassmann and E. J. Kohlmeyer. P. Lebeau found that **copper silicide** readily gives up its silicon to nickel; and H. E. Patten observed that **silicon tetrachloride** has no action on nickel. H. zur Strassen, and P. Bardenhauer and E. Brauns studied the equilibrium between nickel and fused **nickel silicate**; and between nickel and **ferrous silicate.** W. Jander and W. Stamm found that the diffusion of nickel in **magnesium orthosilicate** at 1070° to 1200° is relatively slow. R. H. Gaines studied the corrosion of nickel in contact with **concrete**; and E. Schürmann and W. Esch, in contact with **asbestos.**

Nickel readily alloys with most of the **metals,** and these alloys are discussed below. K. A. Hofmann and H. Hiendlmaier [9] found that the metal is readily attacked by burning **potassium.** According to W. G. Imhoff, nickel resists attack by molten **zinc** more readily than does iron and steel. The action of **alkali hydroxides** has been previously discussed. N. Isgarischeff and I. Mirkin studied the replacement of nickel from soln. of its salts by zinc. N. Kameyama and K. Takahashi studied the dissolution of the metal under the influence of an alternating current. H. Moissan observed that nickel is vigorously attacked when it is melted in contact with **calcium oxide** in air. C. Winkler observed that the nickel available in 1890 had an alkaline reaction, but that the impurity is eliminated when the metal is melted under lime. The metal obtained by reducing the sublimed chloride with hydrogen does not show an alkaline reaction. W. Jander and H. Senf studied the action of nickel on **ferrous oxide.** L. Hackspill and H. J. Pinck found that nickel displaces the alkali metal from **alkali sulphides,** and hydroxides. B. Garre found that the reaction between nickel and **copper oxide** evolves 1434 cals. H. von Wartenberg and W. Gurr studied the action on **zirconia.**

A. J. Hale and H. S. Foster observed that a 0·2N-soln. of **sodium chloride** does not attack nickel appreciably in 28 days; and D. F. McFarland and O. E. Harder, that nickel is not attacked by N-NaCl. R. Krulla's observations are summarized in Fig. 88. L. Davies and L. Wright, C. G. Fink and C. M. Decroly, G. R. White, and H. S. Rawdon and W. A. Tucker discussed the corrosion of nickel by soln. of sodium chloride. According to C. A. Peters, when a soln. of sodium chloride is left over mercury with a nickel wire connecting both liquids, crystalline nickelous hydroxide and sodium hydroxide are slowly formed. A. Coppadoro showed that when a soln. of **potassium chloride** is used as an electrolyte with nickel electrodes and an alternating current, the current yield of dissolved nickel does not exceed 10 per cent.; hydrogen unaccompanied by chlorine is evolved; nickel hydroxide is precipitated; and the electrodes acquire a thin, black film of finely-divided nickel. The addition of potassium hydroxide to the chloride lowers the yield considerably; and an increase in the current density

then causes a further diminution of the yield. The nickel, indeed, assumes the passive state which it presents in alkaline soln. using a direct current. R. Lorenz found that if nickel be the anode in a soln. of potassium chloride, and the cathode be copper sulphide, nickel sulphide is formed. J. T. Travis, and A. J. Hale and H. S. Foster observed that with normal soln. of **calcium chloride,** and of **magnesium chloride,** respectively, 0·05 and 0·08 grm. per sq. dm. are dissolved in 7 days when the soln. are renewed daily, and, respectively, 0·10 and 0·05 grm. per sq. dm. in 28 days when the soln. are not renewed. W. Guertler and T. Liepus found that a soln. of magnesium chloride attacks nickel in the course of 8 days. E. Maass and W. Weiderholt examined the action of dry salts—magnesium chloride, carnallite, *Hartsalz* ($KCl.NaCl.MgSO_4$), potassium chloride, sodium chloride, and magnesium sulphate—and found that the severity of the attack decreases in this order; R. Müller and co-workers, the action of molten **magnesium fluoride;** and J. T. Travis, calcium and magnesium chlorides as well as **zinc chloride.** R. Krulla's observations on the action of soln. of **zinc chloride** are summarized in Fig. 88. G. R. White studied the electrolytic corrosion of nickel as anode in soln. of **sodium sulphate;** and A. Coppadoro observed that if **potassium sulphate** be the electrolyte with nickel electrodes, and an alternating current, some nickel is dissolved, and some nickel hydroxide is formed. A. J. Hale and H. S. Foster found that with a normal soln. of **sodium carbonate** no nickel was dissolved after 28 days' exposure. H. N. Huntzicker and L. Kahlenberg observed that no metal is deposited by clean nickel from soln. of **copper, mercuric, and silver salts,** but the two former are reduced to the cuprous, and mercurous states, respectively. Nickel is normally in the passive state. Activated nickel will reduce potassium permanganate, ferric chloride, nitric acid, etc.; and it can be made to displace cobalt, iron, and even nickel from soln. of their salts. G. Krüss and F. W. Schmidt observed that nickel precipitates gold from a soln. of **gold chloride,** but not quantitatively, owing to a reversal of the reaction, but C. Winkler pointed out that if the nickel be free from alkali, the gold is precipitated quantitatively, and there are no side-reactions. W. Guertler and T. Liepus observed that a soln. of mercuric chloride (1 : 500) is not stable in contact with nickel. O. F. Hunziker and co-workers studied the effect of various salt soln. on nickel; and M. Rabinowitsch and A. S. Fokin, the adsorption of radium-F. R. G. van Name and D. U. Hill studied the rate of dissolution of nickel in acidified soln. of **ferric alum,** and of **ferric chloride**—observed by J. Napier—and also in soln. of **chromic acid.** T. Heymann and K. Jellinek studied the action of nickel on **cobalt salts:** $Co+Ni^{\cdot\cdot}\rightleftharpoons Ni+Co^{\cdot\cdot}$. G. Tammann studied the influence of cold-work on the metallic precipitation from soln. of salts. W. Jander and co-workers studied the action on **nickel sulphide.**

Some reactions of analytical interest.—Soln. of nickel salts of the strong acids give no precipitate with **hydrogen sulphide** in the presence of free acid, but in the absence of free acid, a small proportion of the contained nickel may be precipitated as sulphide; salts of the weaker acids—*e.g.*, the acetate, formate, or monochloroacetate—are more readily precipitated under similar conditions and in the absence of free acid, the greater part of the nickel may be precipitated by the prolonged action of hydrogen sulphide; and if free acids are absent and if sufficient sodium acetate be present, and if the soln. be warm, all the nickel may be precipitated. The reaction was studied by H. Baubigny,[10] A. Terreil, P. J. Robiquet, H. Rose, C. R. Fresenius, and H. W. F. Wackenroder—*vide infra*, nickel sulphide. Hydrogen sulphide in alkaline soln., or **ammonium sulphide** in neutral soln., precipitates the nickel as sulphide. F. Jackson said that the reaction is sensitive to 1 in 64,000. The nickel sulphide is either soluble in or peptized by an excess of ammonium sulphide and particularly so in the presence of ammonia, forming a brown soln. The nickel can be separated from the brown soln. by acidification with acetic acid and boiling; ammonium salts also precipitate the sulphide from the brown soln. Indeed, in the presence of an excess of ammonium salts, colourless ammonium sulphide does not dissolve the nickel sulphide. The subject was

discussed by A. Lecrenier, R. Popper, A. Thiel and H. Ohl, and A. Villiers. Nickel sulphide so obtained is sparingly soluble in dil. mineral acids, but is readily dissolved by conc. nitric acid, or aqua regia, with the separation of sulphur. Ammoniacal soln. of nickel salts give a precipitate of nickel sulphide when treated with **ammonium thioacetate**; and O. W. Gibbs observed that acidic soln. give no precipitate with **sodium thiosulphate,** but with neutral soln. nickel is partially precipitated as sulphide when the soln. is boiled for a long time. C. D. Braun found that ammoniacal soln. of nickel salts give a brownish-red, or if dilute, a yellowish-red coloration in the presence of **potassium thiocarbonate,** K_2CS_3. The reaction was studied by T. L. Phipson, E. D. Campbell and W. H. Andrews, T. Rosenbladt, and G. Papasogli. H. O. Jones and H. S. Tasker observed that **potassium dithio-oxalate** gives a magenta-red with soln. of nickel salts, and the reaction is sensitive to 1 part of metal in 8,000,000 parts of soln. P. Berthier observed that soln. of **potassium sulphite,** not ammonium sulphite, gives a precipitate of a basic salt when boiled with a nickel salt. R. Böttinger studied the action of the ammonium salt. O. Brunck obtained a precipitate of nickel sulphide by adding **sodium hyposulphite** to neutral, ammoniacal, or acetic acid soln. of nickel salts, but not to soln. acidified with mineral acids. A. Martini used cæsium chloride and **sodium selenite** to produce crystals of **cæsium nickel selenite,** $Cs_2[Ni(SeO_3)_2]$, for microscopic tests.

Aqueous **ammonia** precipitates a green basic salt from soln. of nickel salts free from ammonium salts. The precipitate forms a blue soln. with aq. ammonia owing to the formation of a complex salt. If ammonium salts be present no precipitation occurs because of the formation of a soluble complex salt. F. Jackson said that the reaction is sensitive to 1 in 4000. J. C. Roldan found **hydroxylamine** gives precipitates analogous to those obtained with ammonia. Soln. of nickel salts furnish an apple-green precipitate of nickelous hydroxide with soln. of **alkali hydroxide**—the precipitate is insoluble in an excess of the alkali-lye, but is readily dissolved by acids. F. Jackson said the reaction is sensitive to 1 in 16,000. The same hydroxide is precipitated if the soln. be boiled in air, or—unlike cobalt salts—if the soln. contains **hydrogen dioxide, iodine,** or **alcohol,** but if **bromine** water, **sodium hypochlorite, potassium ferricyanide,** or a **persulphate** be present, black nickelic hydroxide is precipitated. These reactions were studied by J. von Liebig, E. D. Campbell and P. F. Trowbridge, and O. Popp. S. R. Benedict observed that potassium periodate gives a precipitate with nickel salts. Soln. of **alkali carbonates** were shown by O. W. Gibbs to give apple-green precipitates of nickel carbonate. F. Jackson said that the reaction is sensitive to 1 in 16,000. Similarly with **ammonium carbonate,** but here the precipitate is soluble in excess owing to the formation of a soluble complex salt. A cold soln. of a nickel salt gives no precipitate with **barium carbonate,** but all the nickel is precipitated as basic carbonate when the soln. is boiled. The reaction was discussed by H. Demarçay, J. N. von Fuchs, and H. Rose.

A bright green precipitate of nickel cyanide is formed with nickel salts on the addition of **potassium cyanide**; the precipitate is readily soluble in an excess of this reagent owing to the formation of a soluble complex salt, K_2NiCy_4. F. Jackson said that the reaction is sensitive to 1 in 2000. The complex salt is readily decomposed by dil. mineral acids with the deposition of nickelous cyanide, and the evolution of hydrogen cyanide. The complex salt, unlike the corresponding salts of manganese and zinc, is not decomposed by ammonium sulphide, but it is readily decomposed by chlorine, bromine, and hypochlorites. Consequently, if the soln. of the complex salt be treated with chlorine or bromine, black nickelic hydroxide is precipitated. A greenish-white precipitate is produced when **potassium ferrocyanide** is added to a soln. of a nickel salt; and the precipitated nickel ferrocyanide is sparingly soluble in hydrochloric acid; yellowish-brown nickel ferricyanide is precipitated by **potassium ferricyanide,** but in the presence of a large excess of ammonia, ammonium chloride, or tartaric acid, a clear brownish-yellow soln. is

produced. These reactions were discussed by F. W. Clarke, A. H. Allen, R. H. Davies, P. E. Browning and J. B. Hartwell, and D. Vitali. P. B. Sarkar and B. K. Datta-Ray recommended **hydrazine thiocyanate** as a precipitant. A. Cavalli obtained a precipitate in ammoniacal soln. with **sodium nitroprusside.**

Dil. soln. of nickel salts give no precipitate with **potassium nitrite,** but dil. soln. of cobalt salts furnish a precipitate. Conc. soln. of nickel salts give a brownish-red precipitate of $K_4Ni(NO_2)_6$—*vide* cobalt. The reaction was studied by O. L. Erdmann, and C. Reichard. P. Berthier observed that a soln. of **sodium phosphate** precipitates apple-green nickel phosphate soluble in acids. Observations on the subject were made by M. S. Cheney and E. H. S. Richards, P Dirvell, and J. Clark. H. Ditz, E. A. Schmidt, L. Lafay, and H. Weil reported that soln. of **potassium chromate** act slowly on neutral soln. of nickel salts in the cold, and rapidly when heated, forming a chocolate-brown precipitate of basic chromate, soluble in acids and in aq. ammonia. A precipitate is formed with 0·000028 grm. of nickel. M. E. Pozzi-Escot observed that in neutral or feebly acid soln. of nickel salts, a sat. soln. of **ammonium molybdate** gives a greenish-white precipitate when warmed to 70°. O. Brunck's reaction with α-**dimethylglyoxime** has been discussed in connection with cobalt; and similarly with M. Ilinsky and G. von Knorre's reaction with α-**nitroso-β-naphthol;** with H. Grossmann and W. Heilborn's reaction with **dicyanodiamidine sulphate;** with K. W. Charitschkoff's reaction with **naphthenic acid;** and with G. Malatesta and E. di Nola's reaction with **1 : 2-diaminoanthraquinone-3-sulphonic acid.** F. W. Atack recommended an alcoholic soln. of α-**benzildioxime,** containing a little ammonia, as a delicate reagent for the detection of nickel with which it forms a red precipitate; B. A. Soule found **fusil-α-dioxime** most sensitive of all. J. L. C. Schröder van der Kolk observed that **aniline** forms characteristic microcrystals in the presence of nickel salts; and P. Ray observed characteristic crystals with **dithio-oxamide.**

The addition of **oxalic acid** to soln. of nickel salts slowly precipitates nearly all the nickel as a greenish-white, pulverulent oxalate; a neutral soln. of potassium oxalate gives a similar precipitate which dissolves in an excess of the reagent. The boiling soln. gives a quantitative precipitate when treated with oxalic acid. The reaction was studied by A. Laugier, O. W. Gibbs, O. Henry, S. R. Benedict, M. Perillon, A. Classon, and G. Nass.

The metallic precipitation of nickel.—E. and A. C. Becquerel observed that **copper** immersed in a soln. of sodium nickel chloride acquires a film of nickel. T. L. Phipson, and Z. Roussin said that **magnesium** precipitates nickel as a black powder from acidified soln. of its salts, and hydrogen is simultaneously evolved; A. Commaille added that nickelous hydroxide gradually separates from neutral soln. of nickel salts in the presence of magnesium. According to A. C. Becquerel, powdered **zinc** precipitates nickel as a black powder from soln. of nickel sulphate or chloride, and some hydrogen is simultaneously evolved; and analogous observations were reported by R. Tupputi, J. L. Davies, and N. W. Fischer. A. Merry observed that zinc precipitates nickel from an ammoniacal soln. of the sulphate. N. N. Beketoff said that **iron** precipitates nickel from soln. of its salts only in the presence of ferrous sulphate.

The physiological action of nickel.—G. C. Gmelin [11] made some observations on the action of nickel salts on the animal organism. According to L. Nathan and co-workers, nickel changes the colour of beer-wort, but has no other injurious action; nickel is slightly injurious to fruit musts; but the polished metal has no injurious action on apples and beer-wort. E. Ludwig, F. Geerkens, and W. S. and S. K. Dziergowsky and N. O. Schumoff-Sieber observed so little action when nickel is used for cooking vessels, that the possibly injurious effects are negligible. K. B. Lehman observed that the solubility of nickel used for cooking vessels is so small that if the whole of the food were cooked in such vessels, the total amount of metal that a man could ingest amounted to 2 mgs. per kgrm. of body-weight. Cats or dogs which had taken quantities of nickel amounting to from 6 to 10 mgs. per

kgrm. for 100 to 200 days remained normal in life, and showed no abnormal post-mortem appearances, although in two cases large amounts of the metal were stored up in the tissues. There is no danger of toxic effects from the use of nickel utensils. E. E. Free observed no toxic effects with nickel on the *Pelargonium* and other plants. A. Riche, M. Nakamura, T. P. Anderson and T. P. A. Stuart, and E. Haselhoff observed the injurious effects of nickel on the growth of plants. According to M. Nakamura, nickel sulphate has no appreciable effect on peas; but A. Niethammer observed a toxic action on the seeds of some other plants; H. Kahho studied the toxic action of nickel salts on plant plasma; and E. Manviloff found nickel salts to be much less poisonous with micro-organisms than is the case with salts of copper and of some other metals. F. Geerkens, H. Schulze, and C. Richet observed that a soln. of 0·018 grm. of nickel chloride per litre prevents the growth of bacteria; and B. Isachenko found that nickel vessels are not suited for growing bacteria—*e.g.*, *Bacillus spermophilinus*. A. Chassevant and C. Richet observed the toxic action of nickel on lactic fermentation; and C. Gerber, the action of nickel salts on the coagulation of milk by proteolytic enzymes.

F. Geerkens, H. Schulze, and C. Richet observed that a soln. with 0·125 grm. of nickel chloride per litre will kill marine fishes in 48 hrs. A. Thomas found that nickel salts are not toxic to Funduli in sea-water, but they are extremely toxic in fresh water. Y. Delage noted that nickel raises the activity of the parthenogenetic *Strongylocentrotus lividus*. F. Wohlwill said that nickel causes capillary hyperæmia of the alimentary tract, and the accompanying nervous symptoms may be due to a direct action on the central nervous system. According to R. H. Chittenden and C. Norris, nickel and cobalt salts have toxic properties on rabbits, but the toxic action is slow, and requires large doses; both cause death by stopping the heart, and also produce enteritis; they interfere with the digestive processes, and produce paralysis of the extremities. They form in a large measure insoluble compounds with the proteids of food, and are excreted with the fæces; the part which enters the circulation is distributed to all parts of the body and ultimately eliminated with the urine. The body temp. is raised, and the peripheral cutaneous vessels are constructed. The spinal cord and brain come first in picking up and storing the metal; the muscular tissues retain more than the liver and kidneys. The lungs and heart also retain high proportions of the two metals. G. Bertrand and co-workers found that nickel and cobalt salts have a definite effect on animal metabolism; and P. Mascherpa, that when administered, orally or subcutaneously, the nickel is absorbed by the organism, and excreted partly by the kidneys, and partly by the intestine. W. Schürmann and T. Baumgärtel examined the precipitation of red corpuscles of sheep by nickel salts; and A. Siegler, the action of nickel on human sera. W. Salant and co-workers found that nickel acetate produces a temporary depression followed by recovery and subsequent stimulation of the intestine; and with a frog's heart, the contractions were less frequent, but more forcible. L. Massol and M. Breton found that the injection of a milligram of nickel sulphate in the brains of a guinea-pig caused death in 5 minutes. According to J. B. V. Laborde and A. Riche, nickel sulphate, injected to the amount of 0·5 to 1·0 grm. per kgrm. body-weight, poisons a rabbit or dog. From 0·5 to 3·0 grm. passed into the stomach produced vomiting and diarrhœa, but it is hardly possible to produce death this way. Nickel is considerably less active than copper, and its usual application is everyday life may be considered uninjurious.

According to C. du Bois, the so-called *nickel dermatitis*, or *nickel itch*, or *nickel rash*, resulting from exposure to the vapours arising from hot nickel-plating baths occurs with 95 per cent. of the persons employed, and the itch passes into acute dermatitis discussed by F. M. R. Bulmer and E. A. Mackenzie, and K. R. Drinker and co-workers. The attack is rare when the plating is done in the cold. Persons who sweat easily are most susceptible to the attack. A first attack does not produce immunity, but rather produces susceptibility to attack. Lanolin on the skin is a preventative. H. W. Armit studied the toxic action of nickel carbonyl.

Some uses of nickel.—Nickel is extensively employed in the manufacture of various alloys with special properties—*e.g.*, monel metal, invar, German silver, nickel steel, heat resisting alloys, permalloy, etc.—*vide infra*, the compounds of nickel with various metals.[12] Nickel coins are current in a few countries—Germany, France, Italy, Switzerland, Mexico, etc.; and nickel-copper alloys (*q.v.*) form the bulk of the nickel coinage of the world.[13] Nickel is employed in the manufacture of resistance wires; in the manufacture of laboratory vessels to resist oxidation, and alkali-lyes [14]—*vide supra*, chemical properties; and in the manufacture of cooking utensils.[15] Nickel is employed in compounding some heat-resisting alloys; wire for sparking plugs, gauze for atmospheric burners of the Méker type, one of the elements of the so-called base-metal pyrometers for rough industrial work, the construction of electrodes in some wireless valves, etc. The use of nickel in heat-resisting and corrosion-resisting alloys was discussed by R. J. McKay,[16] etc. The use of nickel for the manufacture of mirrors has been suggested by E. von Aubel,[17] and by H. Steinach for "facing" cliché. Engraved copper plates, used in preparing prints for pottery decoration, are regularly faced with nickel, or iron, so that they are not so rapidly worn as in the case of softer copper. Nickel is also extensively employed in electroplating various metals—*e.g.*, iron, aluminium, and brass—more readily corroded than is the case with nickel—*vide supra.* The nickel accumulator of E. J. Jungner,[18] and T. A. Edison has been previously discussed. Nickel oxide is employed in tinting colours for glazes and glasses. The particular tint furnished by nickel oxide alone, depends on the composition of the glaze.[19] Thus zinc ferrous glazes furnish a pale blue; magnesian glazes, a yellowish-green; zinc lead glazes, a dark green; barium glazes, a chocolate brown; lead glazes, a medium brown; and alkaline glazes, a light brown colour.

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§ 8. The Atomic Weight and Valency of Nickel

The hydrogen equivalent of nickel approximates 29·5, and its at. wt. is taken to be about 59 because it is in accord with (i) the sp. ht. rule; with (ii) its position in the periodic table; and (iii) with the isomorphous law applied to the complex alkali and nickel sulphates, and the corresponding salts of bivalent iron, and of cobalt. The general properties of iron, cobalt, and nickel—*e.g.*, the absence of salts of tervalent nickel—would place cobalt between iron and nickel in the periodic table, but the at. wt. of nickel is slightly less than that of cobalt, and this fact is regarded as one of the misfits in the periodic table—*vide* **1**. 6, 6, and the at. wt. of cobalt. According to C. G. Barkla and C. A. Sadler,[1] the scattering of the X-rays by nickel is abnormal unless the at. wt. of the element approximates 61·4. The isomorphism of the nickel and magnesium sulphates, $RSO_4.7H_2O$, of the cobalt and nickel chlorides, $RCl_2.6H_2O$, and of the cobalt and nickel nitrates, $R(NO_3)_2.6H_2O$; and the solid soln. of copper and nickel sulphates all support the theory that nickel is *bivalent*. In nickelic oxide, Ni_2O_3, the nickel is presumably *tervalent*, although this oxide does not form characteristic salts. According to

G. Pellini and D. Meneghini, and L. Marino, there are two isomeric forms of nickel dioxide, in one, the nickel is bivalent, and in the other *quadrivalent.* In the nickel tetroxide, NiO_4, of A. Hollard, the element may be *octovalent,* analogous with osmium tetroxide—a subject discussed by T. Curtius. In nickel tetracarbonyl, $Ni(CO)_4$, the nickel may be octovalent, or more likely bivalent—*vide* **5**. 39, 27. D. K. Goralevich considered nickel to be octovalent in the compound $BaO_2.NiO_3$. W. Manchot and co-workers, G. Grube, L. Tschugaeff and W. Chlopin, and I. Bellucci and R. Corelli, supported the assumption that nickel can act as a *univalent* element in compounds of the type Ni(NO)S.R, but not so L. Cambi. P. Ray, R. Vogel, A. A. Blanchard and W. L. Gilliland, F. P. J. Dwyer and D. P. Mellor, A. F. Richter, and E. Thilo discussed the valency of nickel; E. G. Cox and co-workers, the co-ordination number and the planar configuration of complex salts; and W. R. Bucknall and W. Wardlaw, and G. T. Morgan and F. H. Burstall, the stereochemistry of these salts.

In 1826, E. Rothhoff made an analysis of nickel chloride, and from the ratio NiO : AgCl it was concluded that the at. wt. of nickel is 59·05. T. Thomson also studied the subject; and in 1852, O. L. Erdmann and R. F. Marchand obtained 58·2 to 58·6 for the at. wt. calculated from the ratio NiO : Ni determined by reducing the oxide in hydrogen; and in 1856, J. B. Dumas obtained 59·3 in a similar manner. In 1857, E. R. Schneider obtained 58·049 from the ratio Ni : $2CO_2$. J. C. G. de Marignac calculated 58·761 from the ratio $NiSO_4$: NiO=100 : 48·289; H. Baubigny, 58·740 from 100 : 48·280; and P. Schützenberger, 58·676 from the ratio 100 : 48·257. E. von Sommaruga obtained 58·803 from the ratio $2BaSO_4 : K_2Ni(SO_4)_2.6H_2O$: 100·000 : 93·6505. W. J. Russell gave 58·742 from the ratio NiO : Ni=100 : 78·593; J. L. C. Zimmermann, 58·704 from the ratio 100 : 78·582; P. Schützenberger, 58·671, from 100 : 48·257; L. Mond and co-workers, 58·575 from 100 : 78·545; and G. Krüss and F. W. Schmidt, 58·225 from 100 : 78·444 (reduction), and 58·616 from 100 : 78·557 (oxidation). C. Winkler obtained 59·435 from the ratio 2Au : 3Ni=100 : 45·29; 59·030 from the ratio 2Ag : Ni=100 : 27·359; 59·031 from the ratio I_2 : Ni=100 : 23·255; and 59·026 from the ratio 2AgCl : Ni=100 : 20·590. W. J. Russell calculated 58·906 from the ratio Ni : H_2=100 : 3·4211. R. H. Lee obtained 58·025 from the ratio of the salts of brucine, $(C_{23}H_{26}N_2O_4)_6H_6Ni_3Cy_{12}.10H_2O$: 3Ni=100 : 5·7295, and 58·083 from the ratio of the salts of strychnine, $(C_{21}H_{22}N_2O_2)_6H_6N_3Cy_{12}.8H_2O$: 3Ni=100 : 6·595. J. C. G. de Marignac obtained 58·842 from the ratio 2Ag : Ni_2=100 : 60·139; J. B. Dumas, 58·971 from the ratio 100 : 60·199; and W. F. O. de Coninck and M. Gérard obtained 58·57 from the ratio $NiC_2O_4.2H_2O$: Ni; T. W. Richards and A. S. Cushman obtained 58·668 from the ratio 2Ag : $NiBr_2$=100 : 101·270; 58·665 from 2AgBr : Ni=100 : 58·174; and 58·682 from $NiBr_2$: Ni=100 : 26·855. It was thought that the ratios of the first two series should be increased by 0·015 to allow for the presence of a trace of sodium chloride.

G. P. Baxter and L. W. Parsons compared the at. wts. of nickel from terrestrial and meteoric sources by the reduction of the oxide with hydrogen and found for terrestrial nickel 58·70, and meteoric nickel 58·68. The difference is within the limits of experimental error; G. P. Baxter and F. A. Hilton obtained for the ratio $NiCl_2$: 2Ag for terrestrial nickel 0·600730, and for meteoric nickel 0·600726; in the case of the ratio $NiCl_2$: 2Ag, 0·452118 was obtained for terrestrial nickel, and 0·452142 for meteoric nickel. These data gave the same value, *viz.* 58·70 (Ag 107·880, and Cl=34·458) for nickel obtained from both sources. In both cases the meteoric nickel was from the Cumpas meteorite of Sanora, Mexico. G. P. Baxter and co-workers found for meteoric nickel from another source from the ratio $NiBr_2$: 2Ag; 58·696 for terrestrial and 58·694 for meteoric nickel, and from the ratio $NiBr_2$: 2AgBr, 58·694 for terrestrial nickel, and 58·694 for meteoric nickel. These results all agree that there is no perceptible difference in the isotopic composition of terrestrial and meteoric nickel.

G. P. Baxter and co-workers consider that the best representative value for the

at. wt. of nickel is 58·694; F. W. Clarke, and J. A. N. Friend, 58·68; and the International Table for 1931 gave 58·69. M. Gerber, and G. D. Hinrichs discussed some relations of the at. wts.

The **atomic number** of nickel is 28 when that of cobalt is 27 and that of iron is 26. P. Vinassa [2] studied the molecular numbers of nickel compounds; and D. de Barros, the nuclear numbers. According to F. W. Aston, **isotopes** of nickel have been observed with the at. wts. 58, 60, 61, and 62. They were studied by E. K. Plyler, W. Yeh, and J. H. Bartlett. The **atomic disruption** of nickel by the bombardment of α-particles has not been noted by G. Kirsch, H. Pettersson and G. Kirsch, or by J. D. Cockroft and E. T. S. Walton, M. A. Tuve and co-workers, or E. Rutherford and J. Chadwick. E. Matzner said that it is disintegrated by bombardment with Po-Be neutrons. According to N. Bohr, and E. C. Stoner, the **electronic structure** of the atom is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 3, 5) for the M-shell; and (2) for the N-shell. The electronic structure was discussed by A. T. Williams, J. D. M. Smith, M. Kahanovicz, H. Lessheim and co-workers, S. Meyer, G. I. Pokrowsky, P. Ray, W. Heisenberg, W. V. Howard, P. D. Foote, G. Glockler, H. G. Grimm and A. Sommerfeld, W. H. Rothery, H. Collins, F. H. Loring, H. Perlitz, C. D. Niven, H. Eyring and A. Sherman, R. Samuel and E. Markowicz, R. Kruger and W. E. Shoupp, G. N. Lewis, F. H. Newman and H. J. Walke, and H. J. Walke. M. V. Goldschmidt said:

According to R. Ladenburg, and N. Bohr, the similarity in the atomic properties of the members of the iron family of elements is due to the fact that the electrons added as the atomic number increases are not added to the outer layers but pass farther into the interior of the atom. According to the nature and the strength of external chemical action, different numbers of electrons are given up by the atoms, thereby giving rise to the different stages of valency. Thus, in some cases, colourless diamagnetic ions of the noble gas type are formed, and in other cases, coloured paramagnetic ions. The ferro-magnetism and catalytic activity, which are characteristic typical properties of the iron family, can be attributed to these peculiarities of atomic structure. The atoms of the free elements of this family are bound together by strong forces, hence, the melting points are high and the resistance to chemical and mechanical action good.

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§ 9. Intermetallic Compounds and Alloys of Nickel

According to G. von Engeström,[1] W. Flight, and A. G. Charleton, **nickel-copper alloys** must have been used as coinage alloys about 200 B.C., centuries before the discovery of nickel as a metal *sui generis*, because the analyses of some white Bactrian coins bearing images or inscriptions of certain kings of Bactria over the period 246 to 146 B.C., indicate that they contain 77·585 per cent. Cu ; 20·038, Ni ; 0·554, Co ; 1·048, Fe ; and traces of other metals. W. Flight also stated that it is not likely that the coins are forgeries. According to Quintus Curtius, in his *Vita Alexander*, written in the early centuries of the Christian era, the Oxydracæ and Malli presented to Alexander the Great 100 talents of *ferrum candidum* (white iron). A. Cunningham, and W. C. Roberts-Austen believe that the white iron was one of the Chinese alloys of nickel and copper ; and similarly also with the " Indian brass, white as silver," which was mentioned in the Greek *Anthology* by Crinagoris in the first century of our era.

About the middle of the nineteenth century, in 1856, the United States adopted a copper-nickel alloy (88 : 12) for one cent pieces ; but it was later found to be unsuitable. In 1860, the Belgians issued coinages with copper and nickel approximately as 3 : 1 ; and later on a similar alloy was employed for five and ten cent pieces in the United States. According to V. Atanasoff, and W. Flight, the alloy came into use in other countries—Peru, Bulgaria, Honduras, Brazil, Jamaica, Switzerland, Germany, etc. For a time, granules of a white metal occurring in the slags of some disused mines at Suhl, Thuringia, were extracted and sold as *Suhler*

Weisskupfer: the analyses of R. Brandes showed that the alloy contained 8·75 per cent. of nickel, 88 per cent. of copper, etc.

There are many alloys of copper and nickel with special trade names, and others in which copper and nickel are the dominant components. A. F. Cronstedt, T. Bergman, and A. and C. R. Aikin said that copper readily alloys with nickel, and that the products are less ductile than copper, but they are magnetic. The alloys were also mentioned by H. H. Vivian, A. T. Merry, A. Parkes, and H. Elkington. The term *cupronickel* is applied to alloys containing approximately Cu : Ni=80 : 20. The alloy called *constantan* has copper and nickel in the proportions 2 : 3; that sometimes called *nickel bronze* is the coinage alloy 3 : 1, and the alloy with nearly this proportion of the two elements has been called *patent nickel*, an analysis of which showed: 24·14 per cent. of nickel, and 74·71 per cent. of copper; that called *cupronickel* has the proportion about 4 : 1; that called *benedict metal* has the proportion nearly 85 : 15; the tolerance in the government specifications of the U.S.A. are nickel 14 to 16 per cent., and copper, 84 to 86 per cent.; and that called *monel metal*—after A. Monell—has the proportion 3 : 7 or 69 per cent. of copper with up to about 5 per cent. of iron, manganese, and silicon. The composition and preparation were discussed by L. Archbutt, L. Dainelli, R. H. Gaines, E. S. Wheeler, and W. B. Parker. Monel metal is produced from the nickel-copper matte derived from the ores of Sudbury, Ontario, and it is hence termed a *natural alloy*. It varies from 60 to 72 per cent. nickel and the remainder being mainly copper with 0·5 to 6·5 per cent. mainly iron. One specification of the Government of U.S.A. gave as a minimum 60 per cent. nickel, and for castings—Cu, 33; Fe, 6·5; Al, 0·5; and Pb, 0·0 per cent.; whilst for rolling, Cu, 36; Fe, 3·5; Al, 0·5; and Pb, 0·0 per cent. The analyses of H. F. Moore and co-workers gave 26·78 to 27·18, Cu; 68·32 to 68·77, Ni; 2·20 to 2·58, Fe; 1·77 to 1·93, Mn; and 0·15, C. The monel alloy was discussed by M. Fritzemeyer, and M. G. Corson.

The copper-nickel alloys were prepared by N. S. Kurnakoff and S. F. Schemtschuschny by melting the constituent metals in a graphite crucible, but those alloys with over 20 per cent. of nickel dissolve carbon when molten, and reject it as graphite during solidification. H. Behrens added that the molten metal is liable to spit out absorbed gases during cooling, and is also liable to oxidation. He therefore recommended preparing the alloys under a layer of flux consisting of sodium carbonate and borax. The manufacture of the alloys was described by G. Lyons, G. Schüle, and A. Gronningsater and co-workers. W. Stahl observed that the copper oxidizes more readily than the nickel. C. J. Smithells and co-workers prepared the alloys by melting the metals in a magnesia crucible in hydrogen. A. von Kügelgen obtained the alloys by heating a mixture of copper chloride and nickel oxide with calcium carbide. Natural alloys are obtained as in the production of monel metal from the ores of Sudbury, Ontario; and processes of smelting were described by E. Donath, G. Kroupa, and F. W. Martino. Alloys have also been obtained by the simultaneous decomposition of the two metals electrolytically. Thus, D. S. Ashbrook used an electrolytic bath containing sodium phosphate and phosphoric acid, an excess of the copper salt, and a little sulphuric acid. The electrolytic process was also discussed by G. Bruni and M. Amadori, M. Hille and M. Müller, H. D. Hineline and W. B. Cooley, F. Peters, K. Masaki, and L. E. Stout and co-workers; and W. E. Oakley, B. K. Dering, J. E. Hurst, W. F. Graham, J. W. Lehr, W. F. Cochrane, T. S. Fuller, E. T. Asp, C. Philippossian, H. A. Eastick, J. H. Moore, A. Bregman, M. Hengstenberg, H. R. Williams, R. B. P. Crawford and R. D. Snyder, N. C. Marples, M. A. Hall, M. Balzola, J. H. S. Dickenson, E. D. Gleason, and W. T. Griffiths, the preparation and uses of the copper-nickel alloys. R. Lund discussed the uses of the alloys.

L. Mazza and F. Ciani, G. Bruni and D. Meneghini, C. Matano, P. Henry, G. Grube and A. Jedele, A. Jedele, K. Fischbeck, and A. E. van Arkel discussed

the diffusion of nickel into copper and conversely; and T. Peczalsky, the cementation of copper by the vapour of nickel chloride; and diffusion in the copper-nickel system was studied by S. Tanaka and C. Matano, and C. Matano. The equilibrium diagram has been studied by N. S. Kurnakoff and S. F. Schemtschuschny, W. Guertler and G. Tammann, G. H. Gulliver, P. Röntgen and W. Koch, K. Honda and T. Ishigaki, A. L. Feild, V. E. Tafel, O. Bauer and M. Hansen, N. B. Pilling and T. E. Kihlgren, A. Krupkowsky, A. H. Hiorns, L. Tarshish, and L. Guillet. The alloys form continuous series of solid soln. as indicated in Fig. 92 due to W. Guertler and G. Tammann. H. Gautier thought that the 50 : 50 alloys formed a eutectic mixture. The diagram, however, is in agreement with the cooling curves, the microstructures, the hardness, the electrical conductivities, and the thermal e.m.f. of the alloys; as well as with E. Vigouroux's observations on the electrode potentials: no chemical compounds of nickel and copper are known. The magnetic transformation of nickel to the non-magnetic β-form occurs when the temp. rises above 320°. The transition temp. is progressively lowered by additions of copper, so that with 42 per cent. of copper, the transition occurs at 30°. Even in slowly cooled alloys, the solid soln. are not quite homogeneous. P. Chévenard, and A. Krupkowsky observed no sign of the formation of **copper nickelide,** CuNi. B. V. Hill gave for the critical temp. at which the ferromagnetism disappears:

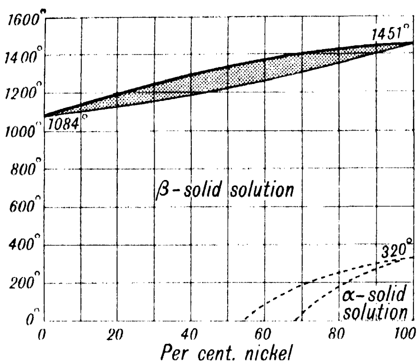


FIG. 92.—Freezing-point Curves of the Nickel-Copper Alloys.

Copper	0	4	8	20	40 per cent.
Hardened . . .	355°	310°	280°	155°	−100°
Annealed . . .	340°	295°	265°	140°	—

W. Guertler and G. Tammann gave for alloys with 89·1, 78·6, 68·2, and 57·9 per cent. of nickel, respectively, 295°, 115°, and 30°; R. Gans and A. Fonseca gave for the critical temp., or Curie point, θ:

Ni .	35	40	45	46	47·5	49	50	55	60	65 per cent.
θ .	−230°	−165°	−100°	−90°	−105°	−105°	−30°	−12°	+20°	+55°

A. Krupkowsky obtained:

Ni	55	60	65	70	75	80	85	90	95	100 per cent.
θ .	−141·0°	−80·4°	−17·0°	40·6°	88·1°	140·1°	196·2°	255·8°	307·9°	368·3°

E. C. Bain showed that the X-radiograms agree with the assumption that the change from one lattice to the other is continuous; in the case of nickel-chromium, iron-nickel, and manganese-copper, there is not a continuous change (*q.v.*). J. H. Long and co-workers, H. Lange, and E. J. Cuy also studied the lattice structure. L. Vegard and H. Dale found that the X-radiograms agree with the assumption that a continuous series of solid soln. is formed. The lattice constant a for 0, 25, 50, 75, and 100 per cent. of copper is respectively 3·530, 3·554, 3·570, 3·591, and 3·610 A. J. Weerts gave the dimensions of the parameters of the face-centred cubic lattice of the copper-nickel alloys shown in Fig. 93. P. W. Bridgman observed that the copper-nickel alloys form a continuous series of solid soln., and that they all have the face-centred

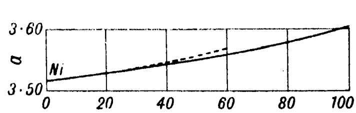


FIG. 93.—Lattice Parameters of the Ni-Cu Alloys.

cubic structure with a varying from 3·605 A. for copper to 3·527 A. for nickel. A. Sacklowsky found for the values of the constant a,

Nickel .	0	10	30	50	60	70	90	100 per cent.
a . .	3·61	3·606	3·595	3·58	3·57	3·56	3·535	3·54 A.

A. Krupkowsky obtained values ranging from a=3·51 A. for an alloy with 57·4 and 67·9 per cent. of nickel. The subject was studied by W. G. Burgers and J. C. M. Basart, E. A. Owen and co-workers, S. Sekito, H. Weiss, W. Rosenhain, H. Lange, E. C. Bain, S. Holgersson, and L. Vegard and H. Dale. F. von Göler and G. Sachs studied the effect of rolling on the lattice structure of monel metal and of constantan; and W. A. Wood, the lattice distortion of cold-drawn wires of constantan.

G. Frick observed that the colour of the Cu : Ni=10 : 1-alloy is copper-red; the 10 : 2-alloy is reddish-white; the 10 : 3-alloy is nearly white; and the 10 : 4 alloy is silvery white. H. Behrens found that the alloy with 10 per cent. of nickel has a reddish or salmon-red colour; the 20 to 25 per cent. nickel alloys are dirty grey; and the 30 per cent. nickel alloys are pale grey. V. E. Tafel said that the copper tint becomes weaker as the proportion of nickel increases, and is scarcely perceptible when 30 per cent. of nickel is present; W. Guertler and G. Tammann said alloys with over 25 per cent. of nickel have the colour of nickel, those with less than 20 per cent. show the characteristic colour of copper. J. A. M. van Liempt, M. Kuroda, and N. S. Kurnakoff and S. F. Schemtschuschny made similar observations. W. T. Griffiths added that the colour with 15 per cent. of nickel is nearly white, and the whiteness and brilliancy are increased as the proportion of nickel rises to 40 to 45 per cent. It is then difficult to distinguish the polished alloy from sterling silver. A further increase in the proportion of nickel makes the alloys less brilliant, and the colour gradually approximates to that of nickel. H. Behrens said that under the microscope, the alloys show crystalline granules with a higher proportion of nickel than is present in the reddish matrix. Hammering and rolling make the alloys fine-grained, and annealing makes them like brass. W. Guertler and G. Tammann found that the alloys rich in copper show needle-like crystals which, as the proportion of copper decreases, change into polygonal crystals. N. S. Kurnakoff and S. F. Schemtschuschny added that the alloys with small proportions of nickel contain rectangular dendrites like copper without a matrix; mixtures with over 40 at. per cent. furnish a mass containing polygonal grains which have more copper about their periphery, but if annealed at 800° to 900°, the structure becomes homogeneous. L. Guillet observed that alloys with less than 50 per cent. of nickel show two distinct structural elements, although E. H. Williams showed that the homogeneous crystals of alloys with up to 70 per cent. of nickel have X-radiograms corresponding with mixtures of crystals of the two elements. A. Krupkowsky studied the microstructure of the alloys etched with a soln. of 1 part of conc. nitric acid, and 2 parts of conc. acetic acid. Observations on the microstructure were also made by V. E. Tafel, T. Hirose, A. H. Hiorns, H. S. Rawdon and M. G. Lorentz, H. F. Moore and co-workers, F. Adcock, and W. B. Price and P. Davidson. O. Bauer and H. Arndt studied the segregation of the alloys.

G. and J. Weir gave 8·87 for the sp. gr. of cast monel metal, and the value for constantan is 8·92 at 18°. E. Grüneisen gave 8·89 for the sp. gr. of the 54 : 46 copper-nickel alloy. D. F. McFarland and O. E. Harder gave for the sp. gr.:

Nickel .	9·29	18·73	28·35	38·10	48·00	58·06	100 per cent.
Sp. gr.. .	8·56	8·76	8·92	8·76	8·78	8·53	8·69

W. C. Ellis and co-workers gave for the Cu : Ni (55 : 45) alloy 8·78; and for monel metal, Cu : Ni : Fe (28 : 70 : 2), 8·94. Z. Nishiyama found the sp. gr., and the

elastic modulus, E kgrms. per sq. cm., of the nickel-copper alloys, between 17·6 and 18·1, to be :

Ni .	0	1	2	5	10	20	25	30 per cent.
Sp. gr. .	8·9369	8·9397	8·9427	8·9449	8·9533	8·9547	8·9533	8·9565
$E \times 10^{-6}$	1·253	1·263	1·273	1·324	1·384	1·457	1·490	1·562

W. M. Corse, and K. Schmidt also studied the sp. gr. of these alloys. N. S. Kurnakoff and S. F. Schemtschuschny found that the scratching hardness of the alloys reaches a maximum when about 50 at. per cent. of nickel is present, and corresponds with the maximum on the e.m.f. curve, and the minimum on the electrical conductivity curve—Figs. 94 and 95. With percentages by weight, they found :

Nickel .	0	2·45	10·00	30·00	48·14	54·80	64·25	85·00	100 per cent.
Hardness	52·0	56·6	63·3	76·6	100·7	101·9	93·6	84·0	72·5

M. Waehlert gave for Brinell's hardness :

Copper .	100	90	80	70	60	50	40	30	20	10 per cent.
Hardness	56	39	45	57	61	64	66	70	74	67

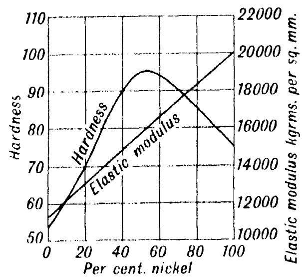


FIG. 94.—The Hardness of the Copper-Nickel Alloys.

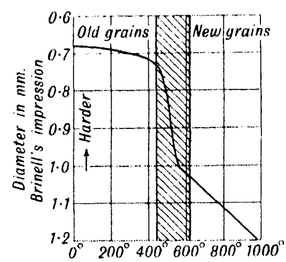


FIG. 95.—The Effect of the Annealing Temperature on the Hardness.

Observations were also made by A. Kussmann and B. Scharnoff, M. Guichard and co-workers, H. C. Dews, T. Isihara, A. Krupkowsky, W. T. Griffiths, and H. W. Brownsdon and co-workers. D. G. Jones and co-workers, W. B. Price and P. Davidson, F. Sauerwald and K. Knehans, T. Usihara, W. A. Mudge and L. W. Luff, M. Kessner, and T. Everts, and N. S. Kurnakoff and J. Rapke found for Brinell's hardness in kgrms. per sq. mm. with a ball 485 kgrms. and 9·52 mm. diameter :

Nickel .	0	10	20	39·7	45·6	59	72	80	100 per cent.
Brinell's .	32·4	43·8	54·1	72·1	81·3	77·3	65·6	74·8	62·8

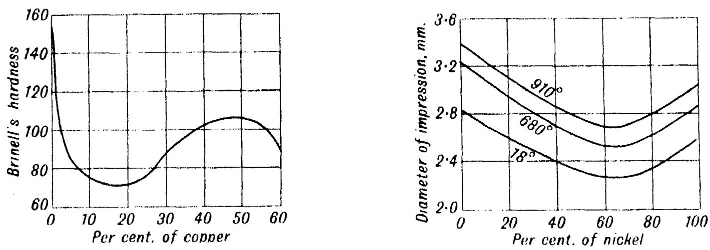
E. Greulich studied the hardening of monel metal by cold-rolling. L. Guillet made some measurements of the rolled alloys and found the hardness was lowered about 5 per cent. on annealing at 750°. T. Hirose found greater differences for the 3 : 1 copper-nickel, coinage alloy, for Shore's scleroscopic hardness :

Annealing temp. . .		500°	600°	700°	800°	900°
Hardness	Before . .	65·0	65·0	63·0	65·0	60·0
	After . .	30·0	21·5	19·5	19·0	17·0

R. Irmann represented the Brinell's hardness of the nickel-copper alloys by the curve, Fig. 96. F. Sauerwald obtained the results summarized in Fig. 97 for the hardness of these alloys at different temp. expressed in terms of the diameter of the impression in mm. made by a ball of 1·256 kgrms. falling 14 cms. F. Adcock's observations on the effect of the annealing temp. on the hardness of the alloys is indicated in Fig. 95. With material reduced 88 per cent. by rolling, and annealed below about 440°, only deformed or old grains are visible ; above 610°, only new grains are present ; and between these temp. both old and new grains are visible. As recrystallization begins to appear there is a marked decrease in the hardness of

the material—*vide infra*, Table IV. W. A. Mudge discussed the resistance of monel metal to denting.

According to W. T. Griffiths, the addition of nickel to copper has a marked effect on the mechanical properties. G. Hughes showed that 2 per cent. of nickel increases the maximum tensile strength slightly, and increases the ductility considerably. The 2 per cent. alloy, cold-worked and annealed, had a maximum stress of 15·2 tons per sq. in.; a 49·0 per cent. elongation on 8 inches; and 78·2 per cent. reduction of



FIGS. 96 and 97.—The Hardness of the Nickel-Copper Alloys.

area. The toughness is also improved, and H. Baucke found that 1·5 per cent. of nickel is sufficient to double the impact value. The combination of ductility with toughness enables these alloys to be cold-worked to an extraordinary degree; and the 4 : 1-copper-nickel alloys are amongst the most ductile non-ferrous metals in commercial use. The hardness and elastic modulus of these alloys increase fairly regularly as the nickel content rises to 50 per cent. N. S. Kurnakoff and J. Rapke's observations on the elastic modulus, E kgrms. per sq. mm., plotted in Fig. 94, show that E increases linearly in passing from copper to nickel whilst the hardness shows a maximum. They found:

Nickel .	0	20	30	45·6	59	72	80	100 per cent.
E . .	11,110	12,590	13,492	14,855	16,710	17,150	18,849	20,100

E. Grüneisen gave 16,555 kgrms. per sq. mm. for the elastic modulus of constantan. Z. Nishiyama's measurements are indicated above. A. L. Kimball and D. E. Lovell gave for the elastic modulus of cold-rolled monel metal $17{\cdot}8\times10^{11}$ dynes per sq. cm., and for the internal friction constant $0{\cdot}79\times10^{15}$ c.g.s. units. Observations were made by C. Heckmann, H. C. Dews, H. J. Tapsell and J. Bradley, G. W. Pierce, D. H. Skeen, E. Krüger, H. Baucke, W. Campbell, A. Schulze, W. B. Parker, R. Müller, and W. A. Mudge and L. W. Luff. C. E. Guillaume found that the addition of nickel to copper raises the elastic modulus approximately in accord with the mixture law; whilst E. Warburg observed a minimum in the elastic after-effect which is smaller than that of the components, and occurs with alloys having nearly 42 per cent. of nickel. T. K. Rose found that the cold-drawn alloy with 25 per cent. of nickel is softened between 500° and 600°.

All the alloys are flexible, very malleable, and, according to K. Styffe, about 50 per cent. harder than copper. Monel metal can be forged hot or cold, brazed, soldered, and welded. T. Fleitmann found that small additions of other metals to cupronickel made little difference to its weldability. Monel metal hardens rapidly when worked cold, and frequent annealing in a reducing atmosphere, free from sulphur, and below 1100°, is necessary. R. J. McKay observed that, under ordinary circumstances, the soft, ductile metal is accompanied by a coarse grain. In drawing, or deformation, the metal gives way in a direction determined by the axis of the grain, and when the grain is large, the effect shows up as depressions on the surface, which may open into cracks extending completely through the sheet. A combined working of the metal and heat treatment gives a metal of high ductility and fine grain. T. Hirose found that some batches of nickel coinage were very brittle, as brittle, indeed, as porcelain or glass, and in some cases could be broken up with the fingers. This brittleness could not be removed by annealing. If the alloy

contains above 0·030 per cent. of oxygen as an impurity, annealing makes it brittle owing to the formation of a network of oxide throughout the mass. The oxygen can be removed by adding some magnesium, cupromagnesium, manganese, ferro-manganese, or cupromanganese to the molten alloy. Sulphur over 0·076 per cent. is harmful. Carbon is not very injurious, but G. A. Boeddicker mentioned coinage alloys which were rendered brittle owing to the separation of graphite which occurs at 650° to 700°.

According to W. T. Griffiths, the 4 : 1 and 3 : 2 copper-nickel alloys when cast and annealed have a maximum tensile stress of 15·3 and 19·4 tons per sq. in. respectively, whilst the percentage reductions of area are respectively 34·0 and 34·5, and the percentage elongations on a 2-in. length are respectively 19·5 and 23. Rolling and annealing improves these qualities considerably. Rods, drawn with 56 per cent. reduction, before and after annealing at 850° to 900° for 15 minutes gave the following results:

		Max. tensile stress (tons per sq. in.)	Elongation (per cent.)	Reduction of area (per cent.)
4 : 1	Hard	33·5	18·0	70·0
	Annealed	21·4	51·0	83·6
3 : 2	Hard	40·9	12·0	56·6
	Annealed	26·7	44·0	73·0

L. Guillet gave for the hard, cold-worked alloy, and the alloy annealed at 750°:

Per cent. Copper		Max. tensile stress (tons per sq. in.)	Elastic limit (tons per sq. in.)	Elongation (per cent.)	Reduction of area (per cent.)	Hardness (Brinell's)
94·4	Hard	12·4	10·4	27	51·8	63
	Annealed	10·4	2·1	44	49·8	53
90·7	Hard	12·2	10·1	14	46·8	61
	Annealed	10·1	1·7	40	57·1	53
85·7	Hard	19·7	19·3	2	11·0	73
	Annealed	9·5	1·4	19	25·2	57
80·6	Hard	20·2	20·2	3	10·2	73
	Annealed	15·0	12·4	15	16·4	60
70·1	Hard	20·0	19·1	6	19·0	88
	Annealed	16·0	14·0	9	18·8	71

The elastic limit of annealed alloys with up to 15 per cent. of nickel is exceptionally low; with higher proportions of nickel, the hardness, tenacity, and elastic limit are raised, and the elongation, and reduction of area are lowered. The effect of annealing on the mechanical properties of cupronickel was studied by L. Aitchison and W. R. Barclay. D. J. McAdam obtained the results summarized in Fig. 98, for a 45 per cent. nickel alloy. Little or no softening occurred until the temp.

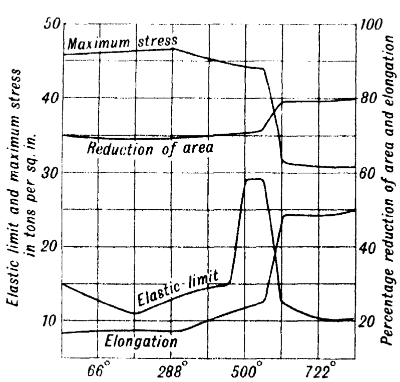


FIG. 98.—The Effect of Annealing on Cold-Rolled 45 per cent. Nickel Alloy.

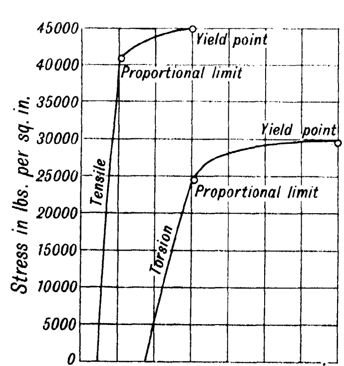


FIG. 99.—Stress-Strain Curves of Hot-Rolled Monel Metal.

exceeded 400°, a little softening occurred at 500°, and at 650°, the metal was completely softened. P. D. Merica and co-workers found for monel metal the results summarized in Fig. 99. In tension, the breaking stress was 94,000 lbs. per sq. in., the proportional limit, 41,300 lbs. per sq. in., and the yield-point, 41,100 lbs. per sq. in.; the elongation was 48 per cent., and the reduction of area, 67 per cent. in 2 inches. In torsion, the breaking stress was 66,200 lbs. per sq. in., the proportional limit was 23,800 lbs. per sq. in., and the yield-point, 66,200 lbs. per sq. in. In 106 test pieces of monel metal, the tensile strength of 1 was up to 80,000; 4 were between 80,000 and 82,500; 6 between 82,500 and 85,000; 22 between 85,000 and 87,500; 35 between 87,500 and 90,000; 23 between 90,000 and 92,500; 11 between 92,500 and 95,000; 3 between 95,000 and 97,500; and 1 was over 97,500—average 88,800. These results show the distribution of the individual values about the mean value, that is, the degree of variation of the individual tests from the average value. G. and J. Weir found the compression tests on hot-rolled, monel metal rods gave for the elastic limit, 45,000 to 50,000 lbs. per sq. in., and for the yield-point, 67,000 lbs. per sq. in. They also gave for the shearing stress at the elastic limit, 31,796 lbs. per sq. in., and at the ultimate load, 79,053 lbs. per sq. in. E. Grüneisen also measured the torsion modulus of constantan; and S. Sato the latent energy due to cold work.

The mechanical properties are well maintained at elevated temp., and in this respect the copper-nickel alloys resemble other nickel alloys, and observations on the subject have been made by M. Ballay, R. Baumann, C. Blazey, D. H. Browne, I. M. Bregowsky and L. W. Spring, W. G. Brombacher and E. R. Melton, C. L. Clark and A. E. White, C. A. Crawford and co-workers, H. C. Dews, C. S. Dunbar, H. A. Eastick, O. W. Ellis, F. A. Fahrenwald, R. H. Greaves and J. A. Jones, L. Guillet, T. W. Hardy and H. H. Bleakney, A. K. Huntington, D. H. Ingall, D. G. Jones and co-workers, G. H. Keulegan and M. R. Houseman, G. Klein, K. R. Koch and C. Dannecker, F. C. Lea, P. G. McVetty and N. L. Mochel, V. T. Malcolm, H. von Miller, E. Osswald, J. S. G. Primrose, G. A. Roush, H. W. Russell and W. A. Welcker, A. Schulze, A. Stansfield, Y. Taji, H. J. Tapsell and J. Bradley, J. F. Thompson, C. Upthegrove and A. E. White, R. G. Waltenberg, E. S. Wheeler and R. J. McKay, W. E. D. Wilkes, and R. Worthington. W. J. de Haas and R. Hadfield studied the properties at —252·8°. The results with the 43 per cent. nickel alloy are summarized in Fig. 100. The material retains the effect of cold rolling up to a comparatively high temp. The strength at 400° of the cold-rolled sheet is as high as that of the hot-rolled sheet at ordinary temp. These tests are made rapidly, and at elevated temp. it is the creep strength that is of prime importance. The dotted lines in Fig. 100 refer to the cold-rolled metal, and the continuous lines to the hot-rolled metal. For the tensile strength of hot-rolled and cast-monel metal, with 28 per cent. copper and 68 per cent. nickel, G. and J. Weir gave the results indicated in Fig. 101. According to G. D. Bengough, the maximum stress, in tons per sq. in., and

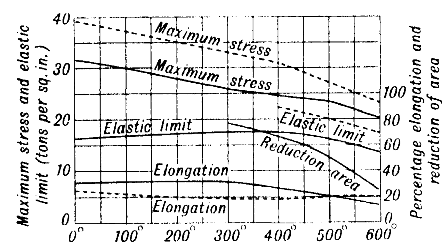


FIG. 100.—Mechanical Properties of the 43 per cent. Nickel Alloy at Different Temperatures.

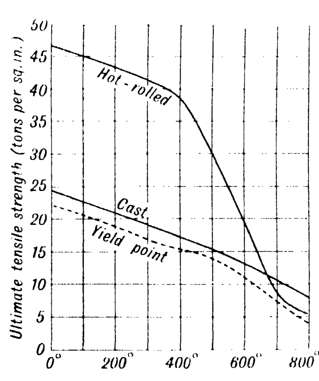


FIG. 101.—Tensile Strength of Monel Metal 68 per cent. Nickel at Different Temperatures.

the percentage elongation of the 80 : 20 nickel-copper alloy when tested at different temp., are as follow :

	17°	300°	580°	675°	685°	760°	795°	950°	1010°
Max. stress . . .	28·7	23·7	12·0	6·7	4·5	2·7	2·6	1·1	1·0
Elongation . . .	27·4	23·5	15·5	20·2	31·2	22·7	26·5	31·2	37·0

The strain-temp. curve differs from those of pure metals ; since the elongation falls off until 650° and then rapidly increases, attaining a maximum at about 700° ; it then falls off up to 750° ; and lastly, rises until at least 1010° is attained. The m.p. of this alloy is 1190°. In the stress-temperature curve the temp. of recuperation is just over 700°. J. Arnott made similar observations. T. K. Rose studied the conditions of annealing needed to render the copper-nickel alloys homogeneous in structure, and suitable for rolling ; and the results for the temp. of annealing, its duration, and the hardness of some alloys are indicated in Table IV. G. A. Boed-

TABLE IV.—THE HEAT TREATMENT OF SOME COPPER-NICKEL ALLOYS.

Metal	Hardness		Lowest temperature at which softening is perceptible	Temperature at which softening is nearly completed	
	Maximum on rolling	Minimum on annealing		in 30 mins.	in < 1 min.
Copper . .	46	13·5	275°	360	400
Nickel . . .	75	36·0	300°	700	—
Coinage bronze .	65	15·5	200°	470	600
80 : 20 . .	64	17·5	300°	550	—
75 : 25 . .	75	23·5	300°	650	—
70 : 30 . .	77	21·5	300°	600	—
50 : 50 . .	87	31·5	400°	700	—

dicker said that with properly annealed alloys the elongation curve should be continuous, *i.e.* it should slowly decrease to about 600°, then increase until the m.p., 1190°, is attained. W. P. Wood studied the torsion modulus of monel metal, and found 8,003,000 lbs. per sq. in.

D. J. McAdam studied the alternating stress tests, and the endurance or fatigue range of some copper-nickel alloys. He found for the 20 per cent. nickel alloy, 8 tons as the endurance limit for the cold-rolled material and 7·2 tons per sq. in. for the metal annealed at 760° for 1 hour ; for the 45 per cent. nickel alloy, he obtained 19·2 tons per sq. in. for the cold-rolled metal, 12·5 tons per sq. in. for the cold-rolled and annealed metal, and 15·4 tons per sq. in. for the hot-rolled metal. The alternating torsion test for the 45 per cent. alloy gave 7·6 tons per sq. in. for the hot-rolled, annealed metal. P. D. Merica and co-workers obtained the results summarized in Fig. 99 for the maximum fibre stress of monel metal with a proportional limit of 36,600 lbs. per sq. in.

D. J. McAdam, H. J. Gough and D. G. Sopwith, and H. F. Moore and co-workers made some fatigue tests on copper-nickel alloys. D. J. McAdam gave the static mechanical tests and the endurance fatigue tests expressed in lbs. per sq. in. of some copper-nickel alloys, including constantan and monel metal. The copper-nickel alloy cold rolled had Cu : Ni=80·34 : 19·23 ; and the hot-rolled alloy, 44·18 : 55·23 ; the constantan had about 53·7 : 44·7 ; and the monel metal 21·28 to 29·54 : 66·78 to 76·66.

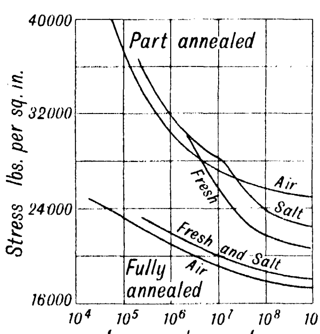
	Copper-Nickel Alloy				Constantan			
	Cold-rolled		Hot-rolled		Cold-rolled		Hot-rolled	
	As received	Annealed	As received	Annealed	As received	Annealed	As received	Annealed
Tensile strength	65,400	62,100	49,900	44,400	103,300	69,400	70,500	70,300
Torsion strength	59,800	58,000	41,700	43,500	65,000	55,700	66,100	60,200
Shearing strength	47,500	47,100	35,300	33,300	59,400	49,900	50,000	50,400
Elastic modulus	—	—	22×10^6	—	—	—	25×10^6	—
Endurance limit	37,800	26,500	20,800	18,000	24,000	43,000	28,000	34,500

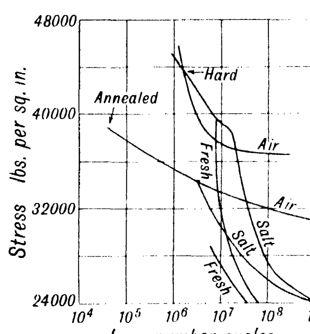
	Monel Metal					
	Cold-rolled		Hot-rolled		Cold-drawn	
	As received	Annealed	As received	Annealed	As received	Annealed
Tensile strength .	97,400	84,400	90,300	77,300	93,500	97,500
Torsion strength .	77,300	—	69,000	66,100	77,000	67,900
Shearing strength .	67,000	61,000	59,400	56,900	66,500	64,300
Elastic modulus .	—	—	25×10^6	—	—	—
Endurance limit .	—	34,000	28,000	38,000	29,500	—

D. J. McAdam observed that the simultaneous action of corrosion and fatigue—corrosion-fatigue—may cause failure at stresses far below the ordinary endurance limit—*vide* the corrosion of iron. With monel metal—with 29·54 per cent. of copper—low and fully annealed—and nickel-copper alloys with 48·37 per cent. of copper—cold-rolled and annealed—and 77·92 per cent. of copper—low and fully annealed—the static, mechanical tests were :

Copper (per cent.)	Anneal	Tensile strength (lbs. per sq. in.)	Elastic limit (lbs. per sq. in.)	Proportional limit (lbs. per sq. in.)	Elongation (per cent. in 2 inches)	Reduction of area (per cent.)
29·54	Low .	127,200	84,500	82,000	20·6	57·8
	Full .	81,900	28,200	25,000	48·9	73·6
48·37	None	85,800	47,500	38,000	34·5	60·3
	Full .	78,000	26,000	22,800	45·5	61·5
77·92	Low .	62,400	34,300	24,700	22·5	68·2
	Full .	47,300	9,200	8,100	50·0	74·7

The corrosion-fatigue expressed in graphs of the stress, and the logarithm of the number of cycles with specimens of monel metal tested in air (fatigue curve), in corroding fresh, carbonate water, and in a corroding river, salt water having about one-third the saline contents of sea-water, and with cycles of 1450 revs. per minute, for the Cu-Ni alloys with 48·37 and 77·92 per cent. copper are summarized in Figs. 102 and 103.





FIGS. 102 and 103.—The Fatigue and Corrosion Curves of the Copper-Nickel Alloys respectively with 48·37 and 77·92 per cent. of Copper.

The resistance of monel metal to shock is very high. G. and J. Weir, and R. G. Waltenberg found that under the Izod impact test, the forged or hot-rolled metal has not been broken, and values up to 114 foot-pounds have been recorded, whereas the value for forged copper is 46 ; cast iron, 1 ; wrought iron, 58 ; and mild steel, 77. Similarly with Charpy's impact test, hot-rolled monel metal gave 153 foot-pounds when cast aluminium gave 9 ; copper bars, 35 ; and chrome nickel steel, 83. H. F. Moore and T. M. Jasper also studied the fatigue strength of monel metal ; and F. Robin, the acoustic properties.

E. Grüneisen, and R. F. Mehl and B. J. Mair gave $0 \cdot 0_6 62$ for the compressibility coeff. of a sample of constantan ; and the value $0 \cdot 0_6 64$ calculated by the mixture rule for Cu : Ni : Mn=55 : 44 : 1 is in close agreement with this. R. F. Mehl

obtained the following results for the compressibility coeff. of alloys of copper and nickel:

Nickel		0	9·8	30·1	50·1	69·6	94·8	100·0 at. per cent.
$\beta\times10^6$	Obs.	0·352	0·357	0·401	0·429	0·450	0·491	0·495
	Calc.	0·352	0·363	0·386	0·411	0·440	0·484	0·495

C. E. Guillaume found that additions of copper to nickel lowered the coeff. of thermal expansion approximately in accord with the mixture law. The mean coeff. of thermal expansion of an alloy with 35 per cent. of nickel is $\alpha\times10^6=14·666+0·00556\theta$, and that of 40 per cent. nickel alloy, $\alpha\times10^6=14·479+0·00448\theta$. By annealing at 100°, some alloys contract 0·002 to 0·003 mm. per metre. A. Krupkowsky gave for the mean coeff. of linear thermal expansion the results summarized in Fig. 105; and for the values of a and b in $l=l_0(1+a\theta+b\theta^2)$:

Nickel		0	10	20	40	50 per cent.
$a\times10^6$	−183° to 217°	15·41	14·82	14·22	13·76	13·13
	18° to 444°	16·35	15·86	15·15	14·48	13·83
$2b\times10^8$	−183° to 217°	1·54	1·62	1·58	1·60	1·63
	18° to 444°	0·74	0·73	0·79	0·90	1·03

Nickel		60	70	80	90	100 per cent.
$a\times10^6$	−183° to 217°	12·90	—	12·41	—	11·86
	18° to 444°	13·92	14·30	13·49	13·85	12·83
$2b\times10^8$	−183° to 217°	1·84	—	1·90	—	2·01
	18° to 444°	0·98	0·69	0·99	0·52	1·03

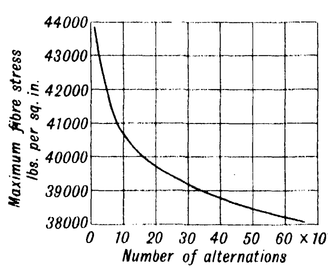


FIG. 104.—Fatigue Tests of Monel Metal.

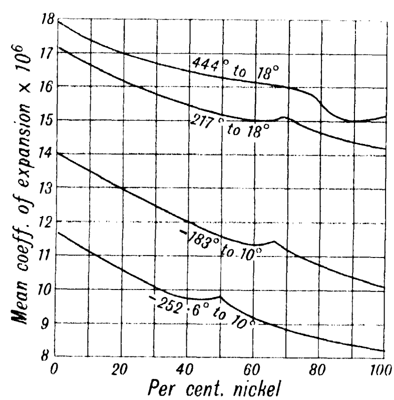


FIG. 105.—The Mean Linear Coefficients of Thermal Expansion of the Nickel-Copper Alloys.

R. F. Mehl gave for the nickel-copper alloys at 35°:

Nickel	0	9·8	30·1	50·1	69·6	94·8	100·0 per cent.
$a\times10^6$	16·9	16·0	15·2	14·4	13·95	13·05	13·0

A. Schulze found for monel metal with Ni : Cu : Fe : Mn, between 20° and

		100°	200°	300°	400°	500°	600°
$a\times10^6$	69·8 : 29·4 : 0·4 : 0·5	13·50	14·10	14·72	15·16	15·52	15·77
	66·1 : 31·0 : 1·8 : 1·0	14·43	14·76	15·17	15·59	15·87	16·10

Measurements were also made by S. Schemtschuschny and S. Pogodin, P. Chévenard, P. Hidnert and W. T. Sweeney, G. Borelius and C. H. Johansson, H. Sieglerschmidt, A. Schulze, H. C. Dews, and C. H. Johansson. F. Henning gave for the expansion of unit length of the alloy with 60 per cent. copper, *viz.* constantan, 0·002489 between −191° and 16°. W. H. Souder and P. Hidnert gave for the coeff. of thermal expansion, a, of monel metal, hot-rolled and annealed:

	25°–100°	100°–200°	200°–300°	300°–400°	400°–500°	500°–600°	25°–600°
a	14·0	15·0	15·9	16·4	17·3	18·1	16·2

L. Holborn and A. Day gave for constantan at 20°, $\alpha=0{\cdot}0_4197$; and at θ°, between 0° and 500°, $l=l_0(1+0{\cdot}0_4148100\theta+0{\cdot}0_840246\theta^2)$. C. H. Johansson gave for the coeff. of cubical expansion, β, at 35°, for nickel-copper alloys with the following atomic percentages of nickel:

Nickel .	0	2·3	9·8	18·4	38·1	50·1	69·6	88·8	94·8 at. per cent.
$\beta\times10^6$.	16·9	16·65	16·0	15·75	14·85	14·4	13·95	13·35	13·05

J. A. N. Friend and R. H. Vallance gave $0{\cdot}0_4177$ for the coeff. of thermal expansion of a nickel-copper alloy between 10° and 100°. W. Jäger and H. Diesselhorst found the thermal conductivity of constantan at 18° to be 0·226 c.g.s. units, and at 100°, 0·268, and the temp. coeff. is 2·36 per cent.; G. and J. Weir say that the thermal conductivity of monel metal is one-fifteenth that of copper; and E. Grüneisen gave 0·484 at 18° for the 54 : 46 copper-nickel alloy. W. C. Ellis and co-workers gave 0·0546 cal. per cm. per sec. per degree for the conductivity of the copper nickel (55 : 45) alloy; and 0·0832 for the monel metal Cu : Ni : Fe=28 : 70 : 2. J. W. Donaldson, and A. W. Smith studied the subject. W. C. Ellis and co-workers gave 0·0546 for the conductivity of an alloy with 55 per cent. of copper. G. F. Sager observed for the thermal conductivity k cals. per cm. per second per degree, the electrical conductivity, K mho; and the ratio R of these constants:

		29°	136°	286°	471°
Copper	k	0·99	1·00	0·95	0·93
	$K\times10^{-5}$	5·55	4·00	2·84	2·06
	$R\times10^9$	5·9	6·1	6·0	6·1
		48°	150°	462°	711°
80 per cent. Cu	k	0·089	0·96	0·150	0·223
	$K\times10^{-5}$	3·54	3·46	3·21	3·02
	$R\times10^9$	7·8	6·5	6·4	7·5
		62°	266°	510°	717°
60 per cent. Cu	k	0·060	0·080	0·120	0·218
	$K\times10^{-5}$	1·99	1·99	1·96	1·92
	$R\times10^9$	9·1	7·4	7·7	11·4
		52°	279°	554°	697°
40 per cent. Cu	k	0·058	0·078	0·132	0·160
	$K\times10^{-4}$	1·88	1·84	1·79	1·74
	$R\times10^9$	9·3	7·7	8·9	9·5
		44°	198°	474°	693°
20 per cent. Cu	k	0·086	0·9	0·128	0·203
	$K\times10^{-4}$	3·36	2·39	2·09	1·96
	R	8·1	8·0	8·2	10·7
		54°	285°	530°	743°
Nickel .	k	0·193	0·164	0·189	0·278
	$K\times10^{-4}$	9·60	4·10	2·74	2·32
	$R\times10^9$	6·1	7·2	8·6	11·8

G. F. Sager, and K. Dittrich studied the application of Wiedemann and Franz's law. B. V. Hill found the specific heat between 20° and 100° of the 4 per cent. copper alloy to be 0·1080; of the 8 per cent., 0·1141; of the 20 per cent., 0·1145; and of the 40 per cent., 0·1003. W. Jäger and H. Diesselhorst gave for constantan 0·0977 at 18°, and 0·1018 at 100°; W. C. Ellis and co-workers, 0·094 for an alloy with 55 per cent. of copper; for the Cu-Ni (55 : 45) alloy, 0·094; and for the Cu : Ni : Fe (28 : 70 : 2) alloy, 0·132. H. Esser and co-workers gave 0·1113 for the sp. ht. of the alloy with 20 per cent. of nickel. K. E. Grew, K. Honda and M. Tokunaga, W. F. Hampton and J. H. Mennie, and L. Rolla studied the sp. ht. of the alloys. A. Eucken and H. Werth found the at. ht. of constantan for constant press. and constant vol., and for Debye's constant: Θ—the x of **1.** 13, 15—

T° K.	15·20°	17·40°	76·00°	121·31°	188·2°	201·97°
C_p .	0·05780	0·07108	2·522	4·137	5·130	5·335
C_v .	0·05780	0·07108	2·515	4·108	5·064	5·255
Θ .	305	325	347	345	330	324

Observations on the f.p. of the alloys were made by C. T. Heycock and F. H. Neville, N. S. Kurnakoff and S. F. Schemtschuschny, V. E. Tafel, B. V. Hill, H. Gautier, W. Guertler and G. Tammann, etc.—*vide supra*, Fig. 120. The m.p. of monel metal is given as 1360°. G. D. Bengough gave 1190° for the m.p. of the 80 : 20 Ni : Cu-alloy. W. P. White found the latent heat of monel metal to be 68 cals. per gram. B. V. Hill calculated for the latent heat of the magnetic transformation 4·48 cals. per gram. I. Obinata studied the rate of cooling of cupronickel from 900° to 200° in various quenching media; and J. A. M. van Liempt and J. A. de Vriend, the time of melting thin fuses.

H. Rubens studied the temp. coeff. of the emissive power of constantan; M. Luckiesh, and I. Langmuir of monel metal; P. Bergmann and W. Guertler, the reflecting power; H. Lowery and co-workers, the optical properties; and H. Koto, the reflection of ultra-violet rays. W. Coblentz found the reflecting power, R, of monel metal, for light of wave-length, λ, in μ=0·001 mm., to be:

λ . .	0·45	0·50	0·70	0·90	1·00	2·00	3·00	4·00μ
R . .	56·5	57·8	63·7	70·0	72·3	83·8	88·7	91·0 per cent.

E. Hagen and H. Rubens gave for constantan—Cu : Ni=60 : 40, and for patent nickel—Cu : Ni=75 : 25 and 80 : 20:

λ . .		0·65μ	1·0μ	2·0μ	4·0μ	6·0μ	8·0μ	10·0μ	12·0μ	14·0μ
R	60 : 40 .	70·0	72·4	82·3	88·3	(91·1)	92·7	94·0	94·0	94·2 per cent.
	75 : 25 .	71·0	72·6	83·5	91·4	(92·2)	93·5	93·0	93·0	92·6 ,,
	80 : 20 .	73·0	75·0	84·1	92·1	(92·1)	92·5	92·6	94·3	93·4 ,,

P. Drude, and J. T. Littleton gave for light of wave-length 5893:

Nickel . . .	25	35	40	50	60	75 per cent.
K	3·32	3·46	3·08	3·61	3·29	3·15
μ	1·55	1·61	2·09	2·33	2·12	2·01
R	64·0	66·6	56·2	61·0	58·7	57·7 per cent.

W. T. Griffiths said that the sp. electrical resistance of the copper-nickel alloys increases with the proportion of nickel, being about 3 micro-ohms for the 2 per cent. nickel alloy; 28 micro-ohms for the 20 per cent. alloy, and it reaches a maximum of 51 micro-ohms for the 50 per cent. alloy. Many alloys of nickel and copper are used as resistance wires—*e.g.*, constantan. Those containing 40 to 45 per cent. nickel have the valuable property of having almost a zero temp. coeff. P. R. Kosting's results for the sp. electrical resistance in micro-ohms per cm. cube, and for the temp. coeff. of the resistance in ohms per ohm per degree $\times 10^4$ are summarized in Fig. 106. A. A. Somerville's results for constantan and monel metal are

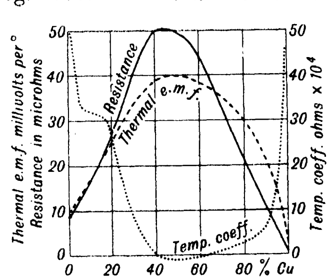


FIG. 106.—The Electrical Resistance of the Nickel-Copper Alloys.

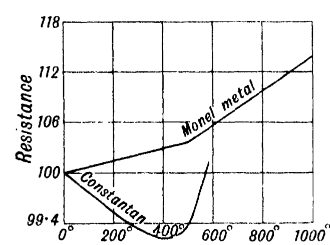


FIG. 107.—The Effect of Temperature on the Electrical Resistances of Constantan and Monel Metal.

summarized in Fig. 107. Measurements were made by M. A. Hunter and A. Jones, and S. Ikeda. Several other alloys were also examined. R. S. J. Spilsbury found that the variability of the temp. coeff. of commercial constantan wires is due to the effect of drawing; the temp. coeff. becomes more negative with progressive drawing. N. S. Kurnakoff and S. F. Schemtschuschny observed a minimum in the

electrical conductivity curve with about 50 per cent. nickel. The observed values for the conductivity, mho$\times10^4$, at 0° are :

Nickel	0	10·04	20·04	41·25	50·84	56·37	62·02	89·46	100
Mho$\times10^4$	65·3	6·8	3·8	2·0	1·93	1·90	1·94	5·3	8·1

The reciprocals are plotted in Fig. 106. A. Krupkowsky gave for the resistance in micro-ohms, *i.e.* $R\times10^6$, and the temp. coeff. of the resistance, a :

Ni		0	10	20	40	60	70	80	90	100 per cent.
$R\times10^6$	Quenched	1·565	14·13	27·76	47·40	53·09	48·00	27·36	19·48	8·84
	Annealed	1·565	14·80	28·55	48·01	52·48	48·80	27·53	20·35	8·03
$a\times10^4$	Quenched	42·10	6·89	2·24	0·14	2·55	15·52	27·93	36·64	57·70
	Annealed	42·10	4·53	3·09	0·10	1·71	14·46	27·53	34·82	62·00

A. Krupkowsky and W. J. de Haas observed that the electrical conductivity curve of the copper-nickel alloys, annealed in vacuo at 750° to 780°, is characteristic of pure mixed crystal and shows no appreciable curvature at the transition from ferro- to paramagnetic alloys. It shows a wide rounded minimum at a composition near to 55 per cent. Ni. In the temperature-conductivity curves for some alloys a point of curvature occurs which corresponds exactly with the Curie points of the alloys, which, for alloys containing 43·45, 48·40, and 57·54 per cent. Ni, are respectively −247°, −196°, and −97°. A strong increase in the coefficient of resistance occurs with those alloys in which the transition from the ferro- to the paramagnetic state takes place. Negative resistance coefficients between −258·4° and −252·5° were obtained with alloys containing between 12 and 35 per cent. Ni. A. Krupkowsky's observations on the effect of temp. on the resistance of these alloys are summarized in Fig. 108—*vide supra*. Observations were made by A. Schulze, G. Borelius, H. Rolnick, R. Schenck, S. Kimura and Z. Isawa, G. Wuckel, N. A. Schalberoff, and S. A. Pogodin and E. M. Lakarenko. H. Schimank obtained for constantan at 0° K., $R_0=2·847$ ohms, and for the ratio $R_T : R_0$, at

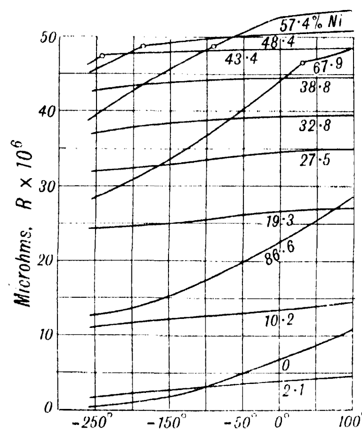


FIG. 108.—The Effect of Temperature on the Electrical Resistance of the Nickel-Copper Alloys.

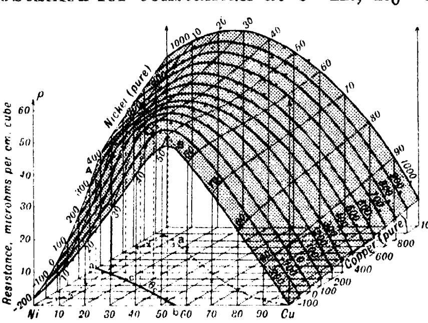


FIG. 109.—The Electrical Resistance of the Copper-Nickel Alloys.

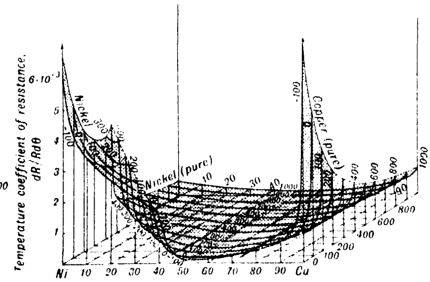


FIG. 110.—The Temperature Coefficient of the Resistance of Nickel-Copper Alloys.

273·09°, 196·7°, 87·3°, and 20·2° K., 1·0000, 0·9982, 0·9898, and 0·9784 respectively. M. A. Hunter and co-workers measured the resistance of monel metal at 20° in ohms per mil. ft., and assuming this value unity, they found that the resistances, R, at different temp. were :

	20°	50°	100°	200°	400°	600°	800°	1000°
R	1·0000	1·0629	1·1508	1·217	1·294	1·384	1·488	1·626

There is a transformation point at 100°. P. Chévenard applies the term *anomalie* to the transformations which do not necessarily correspond with an allotropic change but which show themselves by a break in the continuity of the curve. The results for the resistance, R, of the copper-nickel alloys are summarized in Fig. 109, where A represents the break in the curve for nickel, and the curve a denotes the amplitude of the anomaly. The corresponding values for the temp. coeff., $dR/R.d\theta$, are summarized in Fig. 110. P. W. Bridgman measured the effect of pressure on the electrical resistance, R, of the copper-nickel alloys at 25°, and found for the relation $\delta R/R_2 = ap + bp^2$, where a and b are constants :

Nickel . . .	0	0·145	1·50	4·58 per cent.
a	$-0{\cdot}0_5203$	$-0{\cdot}0_5180$	$-0{\cdot}0_5119$	$-0{\cdot}0_694$
b	$0{\cdot}0_{11}96$	$0{\cdot}0_{11}71$	$0{\cdot}0_{11}38$	$0{\cdot}0_{11}21$
Nickel . . .	8·23	12·9	24·3	50·8 per cent.
a	$-0{\cdot}0_6745$	$-0{\cdot}0_6725$	$-0{\cdot}0_6700$	$-0{\cdot}0_6685$
b	$0{\cdot}0_{11}10$	$0{\cdot}0_{11}10$	$0{\cdot}0_{11}12$	$0{\cdot}0_{11}10$

The results are summarized in Fig. 111. W. Guertler measured the electrical conductivity in terms of the vol. per cent. of nickel in the alloys. K. Feussner, and K. Feussner and St. Lindeck observed that the sp. resistance increases proportionally as the nickel-content rises to 30 per cent., it increases more rapidly as the nickel-content increases to 46 per cent., it then remains nearly constant as the nickel-content rises to 62 per cent., and it then falls nearly proportionally with the contained nickel. The temp. coeff. of the resistance, a, falls slowly as the proportion of nickel increases until it acquires a negative value with about 40 per cent. of nickel, and with higher proportions of nickel, the temp. coeff. increases again. Thus, expressing the sp. resistance, R, in micro-ohms per cm. cube :

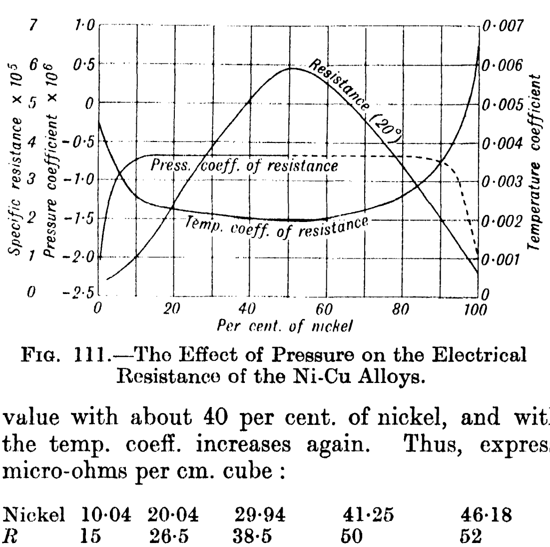


FIG. 111.—The Effect of Pressure on the Electrical Resistance of the Ni-Cu Alloys.

Nickel	10·04	20·04	29·94	41·25	46·18	49·36	62·02	89·46	93·66
R	15	26·5	38·5	50	52	51·5	51·3	20·0	18
a .	0·055	0·0025	0·00013	−0·000014	−0·00005	0·00004	0·0002	0·00285	0·00284
E.m.f.	21·8	29·1	33·5	37·9	39·3	35·8	35·0	26·9	23·5

P. W. Bridgman, W. H. Stannard, J. Strauss, A. A. Somerville, S. F. Schemtschuschny and co-workers, and C. Liebenoff also studied the sp. resistance and the temp. coeff. B. V. Hill observed that the temp. coeff. of the 4, 8, and 20 per cent. copper alloys becomes less and less as the temp. rises to the transition point, when it remains nearly constant. In the 20 per cent. alloy, the change is sharp, and corresponds closely with the transition point. H. le Chatelier found that the electrical resistance of the 81 per cent. nickel alloy changes from 0·485 at 0° to 0·473 between 300° and 700°, and for a wire of 1 mm. thickness, and 80 per cent. of copper, he gave $R = 0{\cdot}420 + 0{\cdot}000110\theta$ ohm. The electrical conductivity of constantan was measured by G. L. Gray, E. Sedström, P. Chévenard, W. Jäger and H. Diesselhorst, and E. L. Lederer. G. Niccolai found the electrical resistance of constantan at 400° is to that at −189° as 1·052, and it is changed by annealing. Taking R in absolute units, he found for constantan at

	400°	250°	200°	150°	100°	50°	0°	−50°	−100°	−150°	−189°
R	44,800	44,800	44,778	44,725	44,621	44,405	44,133	43,808	43,423	42,975	42,604

W. C. Ellis and co-workers gave for the electrical conductivity of the Cu : Ni(53 : 45) alloy, $k \times 10^{-5} = 0.2032$ mho; and for monel metal with Cu : Ni : Fe(28 : 70 : 2), $k \times 10^{-5} = 0.2346$ mho. The Wiedemann-Franz law does not apply. A. Schulze found that the electrical resistance of nine varieties of monel metal ranged from $0.0_4 4269$ to $0.0_4 4865$ at 20°, and the temp. coeff. between 15° and 25°, from 0·001639 to 0·002128. Up to 100°, the Curie point, the electrical resistance increases rapidly with temp., and above 100° slowly such that the temp. coeff. above and below 100° are respectively 1·75 and 0·4 per cent. H. D. Arnold and L. W. McKeehan observed that the effect of tension and magnetization is to raise the electrical resistance about 2 per cent. in either case, but there are differences in the initial stages. U. Fischer gave for the press. coeff. of the electrical resistance, R, of constantan, $-10^7 dR/Rdp = 7.6$ at 273·1° K.; 4·7 at 198° K.; 5·2 at 81° K.; and 6·6 at 20·3° K. N. F. Mott measured the effect of magnetization on the conductivity; and H. Rolnick, the effect of tension on the electrical resistance of constantan; and H. R. Williams, the effect of tension and magnetization on the resistance of monel metal. The potentials of constantan in aq. soln. of potassium chloride of different acidities were measured by F. Vles and A. Ugo.

The copper-nickel alloys exhibit a comparatively high thermoelectric effect combined with a fairly straight e.m.f.—temp. curve, and the alloys have been used for the so-called base metal pyrometers. P. R. Kosting's values for the thermoelectric force of the alloys against platinum, in microvolts per degree, are summarized in Fig. 106 along with the resistance curves. K. E. Grew measured the effect with platinum, and there is a marked break in the curve at 360°—see nickel. K. Feussner, and K. Feussner and St. Lindeck obtained the results indicated above, and in Fig. 112, for the thermoelectric force in microvolts per degree of copper against nickel-copper alloys. Analogous results were obtained by E. Sedström. W. Rohn measured the thermoelectric force of the alloys against platinum; and E. Meschter observed maxima for $dE/d\theta$ against θ at 100° and at 87°. F. E. Bash's observations on the thermoelectric force of nickel-copper alloys against platinum are indicated in Fig. 112. Observations were made for the constantan-copper thermocouple by W. Jäger and H. Diesselhorst, F. G. Keyes and co-workers, W. P. White and co-workers, P. Chramoff and L. Lwowa, L. Rolla and co-workers, E. H. Hall, A. L. Norbury, L. J. Neuman, J. Galibourg, W. Broniewsky, J. C. Southard and D. H. Andrews, O. Walger and F. R. Lorenz, T. Kousmine, and F. G. Wick. The results of L. H. Adams and J. Johnston for temp. from 0° to 200°; of L. Holborn and co-workers for temp. above 200°, and −80°; and of H. K. Onnes and G. Holst for other low temp., are for the e.m.f. of the constantan-copper couple E in millivolts:

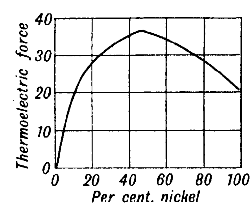


FIG. 112.—Thermoelectric Effect of Copper against the Copper-Nickel Alloys.

	−269·80°	−192°	−80°	0°	25°	50°	75°	100°	200°	300°	400°	500°
E .	−6·630	−5·320	−2·7	0	0·979	2·013	3·096	4·227	8·8	14·1	19·9	26·3

P. W. Bridgman represented the results between 0° and 300° by $E \times 10^6 = -38.5\theta - 0.0445\theta^2$ volt. A. Schulze found that the thermoelectric force of copper against monel metal is positive, and up to 600°, varies linearly with temp. A. W. Smith and J. Dillinger found the thermoelectric force of the copper-permalloy couple is lowered by a magnetic field; and on permalloy with 78 per cent. nickel, tension decreases the thermal e.m.f.; with 81 per cent. nickel, the couple is insensitive to tension; and with 84 per cent. nickel, tension decreases the e.m.f. for low magnetic fields, but with H over 10 gauss, there is an increase in the e.m.f. L. Holborn and co-workers gave for the silver-constantan couple:

	0°	100°	200°	300°	400°	500°	600°
E .	0·00	4·12	8·84	14·10	19·77	25·79	32·15

and for the molybdenum-constantan, and the tungsten-constantan couples:

	−185°	−80°	0°	100°	300°	500°	700°	900°
E (Mo) . .	—	—	0·00	4·66	16·53	30·73	46·65	54·98 (800°)
E (W) . .	−4·66	2·57	0·00	4·21	15·29	28·89	44·75	60·00
E (Fe) . .	−7·0	−3·4	0·00	5·1	15·5	25·7	36·2	47·9

The values for iron are due to C. Dannecker, and slightly higher values were obtained by F. Hoffmann and A. Schulze. For O. L. Kowalke's observations on the cobalt-constantan couple, *vide supra*, cobalt. For the platinum-constantan couple, G. Reichard gave —3·30 millivolts at 100°; W. Jäger and H. Diesselhorst, —3·44 millivolts; E. Wagner, —3·47 millivolts; and K. Feussner and St. Lindeck, —3·04 millivolts. W. Rohn also studied the thermoelectric force of the copper-nickel alloys against platinum; R. Wiebe and M. J. Brevoort, against copper. H. Herl obtained for a couple of constantan and an alloy of 100 antimony, and 57 zinc, 0·13 volt at 480°; and A. G. Warren and F. Murphy, for a constantan-bronze couple, 0·35 to 0·52 microvolt per degree. Observations on the subject were made by W. Hoskins, and C. B. Thwing. A. Krupkowsky's observations on the thermoelectric force of the nickel-copper alloys against lead are summarized in Fig. 113. P. W. Bridgman obtained for the lead-constantan couple $E\times10^6=-34{\cdot}76\theta-0{\cdot}0397\theta^2$ volt; and for the effect of pressure, *p*, in kgrms. per sq. cm. on the thermal e.m.f., $E\times10^6$ volts, of a couple composed of uncompressed constantan, and of the same metal at a press. *p*, when the cold junction is at 0°, he gave:

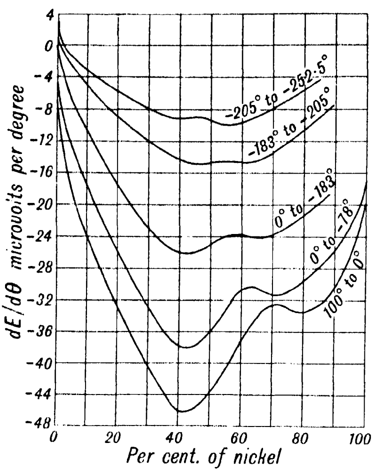


FIG. 113.—The Thermoelectric Force of the Nickel-Copper Alloys against Lead.

		10°	20°	40°	60°	80°	100°
p	2,000 . .	0·55	1·11	2·26	3·45	4·68	5·95
	6,000 . .	1·71	3·44	6·94	10·51	14·14	17·84
	12,000 . .	3·35	6·75	13·67	20·77	28·03	35·47

The press. coeff. between 0° and 100° up to 12,000 kgrms. per sq. cm. is $0{\cdot}0_6409$. E. Wagner obtained $dE/d\theta=26{\cdot}4$ to $31{\cdot}1\times10^{-12}$ volt per degree for a couple of uncompressed and compressed constantan at 300 kgrms. per sq. cm. A. Krupkowsky and W. J. de Haas found that the thermoelectric coeff. of the copper-nickel alloys, annealed in vacuo at 750° to 780°, show two minima in the temp. ranges —250° to —252·5° and —183° to —0°, and one minimum in the range —205° to —183°. The maximum occurring between the two minima corresponds exactly with the Curie point. The thermoelectric coefficient decreases markedly at low temp. and seems to approach zero at 0° K. The linear dilation coefficient curves of these alloys show slight maxima, which with decreasing temp. occur at increasingly small percentages of nickel. The inflexion points of the resistance curves and the maxima of the thermoelectric coefficient curves meet with decreasing temp. on the curve of magnetic transition, which is a straight line which on extrapolation cuts the composition axis at a point corresponding with an alloy containing 41 per cent. of nickel.

E. Sedström measured the Peltier effect of the nickel-copper alloys. P. Czermak found the Peltier effect of constantan against lead, tin, cadmium, and mercury tube quite regular up to the m.p. of the latter metals; for lead he gave for the Peltier effect *P* microcals. per coulomb, 1·90 at 0°=2·73 at 100°; 3·6 at 200°; and 4·4 at 300°. For the copper-constantan couple, E. Beck gave $P=2{\cdot}436$ at 15·5°; and G. Borelius, 2·80 at 0°; and for the iron-constantan couple, P. Czermak

gave 3·1 at 0° ; 4·1 at 100° ; and 5·5 at 200° ; whilst E. Beck gave 3·25 at 14°. M. A. Hunter and A. Jones measured the thermoelectric force of constantan against copper, and the results are indicated in Fig. 107 in connection with nickel. W. H. Keesom and co-workers, and E. Jänecke measured the thermoelectric force of the alloys against an alloy of gold and silver. K. Fuji studied the constantan-manganin couple.

P. W. Bridgman gave for the Peltier effect, P volt, of the lead-constantan couple, $P\times10^6=(-34\cdot76-0\cdot0794\theta)(\theta+273)$ volts ; and E. Lecher obtained for the effect with the constantan-iron couple, $3\cdot4\times10^{-3}$ gram-cals. per coulomb at 20°. P. W. Bridgman gave for the Peltier heat effect between the compressed and uncompressed metal in joules per coulomb $\times10^6$, for pressures, p kgrms. per sq. cm. :

	0°	20°	40°	60°	80°	100°
p 2,000	15	17	18	20	22	24
p 6,000	46	51	55	60	65	70
p 12,000	90	99	109	119	130	140

P. W. Bridgman gave for the Thomson effect, σ volts per degree, with the lead-constantan couple $\sigma\times10^6-0\cdot0794(\theta+273)$ volt ; and E. Lecher showed that the variation of the effect with temp. can be represented by a line of the second order. E. Lecher gave for the Thomson effect, σ microvolts per degree, with constantan, $\sigma=-23\cdot0$ at 0° ; $-19\cdot9$ at 200° ; and $-13\cdot7$ at 400° ; whilst G. Borelius gave $\sigma=-25\cdot5$ at 17° ; $-24\cdot9$ at 19·5° ; and $-25\cdot6$ at 25°. H. E. Smith found the Thomson effect with constantan decreases with tension by becoming less negative until the elastic limit is reached, after which it increases. H. R. Nettleton studied the Thomson effect with constantan. P. W. Bridgman found for the effect of press. p kgrms. per sq. cm. on the Thomson effect with a couple of compressed and uncompressed constantan to be in joules per coulomb per degree $\times10^8$:

	0°	20°	40°	60°	80°	100°
p 2,000	2·7	2·9	3·1	3·3	3·5	3·7
p 6,000	4·6	5·0	5·3	5·7	6·0	6·4
p 12,000	12·6	13·5	14·4	15·3	16·2	17·2

A. M. Portevin obtained the values summarized in Fig. 114 for the potentials of the nickel-copper alloys in dil. sulphuric acid. A. J. Allmand and H. J. T. Ellingham showed that the potential curve of the iron-copper alloys is quite different from that obtained with alloys having components which form solid soln. R. Kremann pointed out that when a binary alloy, with components occupying different positions in the electromotive series, is dipped in a corrosive soln., the nobler metal will dissolve less readily than the other, and will therefore inhibit or retard the corrosion of the alloy ; and G. Tammann showed that with alloys in which the concentration of the nobler metal exceeds a certain value, depending on its mol. wt., it protects the less noble constituent. Some discrepancies with the nickel alloys are accounted for by the tendency of nickel to become passive, and when this occurs the potential increases towards the more noble values. L. Nowack found that the range of chemical activity of solid soln. of nickel-copper alloys is 0·34 mol. nickel for K_2S_2 soln. ; 0·26 mol. for sodium or potassium hydroxide, or for alkaline soln. of hydrogen dioxide or of sodium tartrate ; 0·61 for soln. of ammonium or sodium persulphate ; 0·89 for soln. of silver nitrate ; 0·76 for soln. of silver or copper sulphate ; 0·74 for soln. of copper acetate ; 0·86 for soln. of copper nitrate ; 0·52 for mercuric cyanide ; 0·76 for mercuric nitrate ; and 0·89 for mercurous nitrate. Anodic evolution of oxygen occurs with alloys having from 1·0 to 0·48 mol. nickel. The voltage at which a stronger and continuous opposing current flows is the same for alloys with up to four-eighths mol. of nickel.

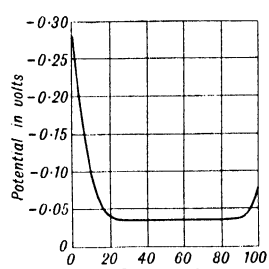


FIG. 114.—The Potentials of the Nickel-Copper Alloys.

N. T. Gordon and D. P. Smith found that the e.m.f., E millivolts, of copper-nickel alloys in an electrolyte containing xN-Cu plus $(x-1)N$-Ni, when that of a calomel electrode is 0·5642 volt at 25° :

Copper		6·8	10·9	65·5	74·3	83·4	94·7 per cent.
E	$x=0·3$	563·5	564·2	574·0	579·0	584·0	585·2
	$x=0·1$	545·2	556·0	564·5	564·5	571·0	568·5
	$x=0·05$	535·3	541·2	558·5	557·0	561·0	561·0
	$x=0·01$	502·2	518·5	544·5	539·0	541·8	537·2

The potential changes rapidly for some time after immersion, but after some hours a steady value is reached, which afterwards remains constant within 3 millivolts during the period of observation. It is found that carefully annealed specimens give the most constant results, and although there are no regular differences between the steady potentials of surfaces annealed and those treated with emery, yet the latter exhibit greater accidental variations. Polished surfaces have a greater tendency to give ions to the soln. With alloys from a given ingot, and also with ingots of a similar composition, it was found that the steady potential is definitely determined by the composition of the electrolyte. E. Vigouroux observed no critical points on the e.m.f. curves of these alloys in acids, and inferred accordingly that no chemical compounds exist. A. Krupkowksy obtained for the maximum and minimum values of the e.m.f. of the nickel-copper alloys dissolving in a normal soln. of ammonium nitrate containing 1 per cent. each of nickel and copper nitrates, the results summarized in Fig. 115. The other electrode was carbon. F. Vles and A. Ugo measured the electrode potential of constantan in a soln. of potassium chloride; and O. Bauer found the potential of a 1 : 1 copper-nickel alloy in a 1 per cent. soln. of sodium chloride against a normal calomel electrode to be —0·197 volt at the start; —0·174 volt after 1 hr.; and —0·100 volt after 120 hrs. A. L. Norbury studied the thermoelectric force against copper. J. Königsberger and G. Göttstein gave for the Hall effect with constantan, $R\times10^6=-910$ at 18°; and H. Zahn, —900 at 18°. J. Obata, and A. W. Smith studied the effect of temp. on the Hall effect of monel metal; and L. Belladen, the cathodic disintegration.

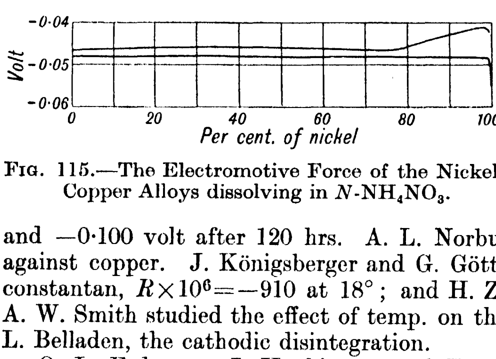


FIG. 115.—The Electromotive Force of the Nickel-Copper Alloys dissolving in N-NH_4NO_3.

O. L. Erdmann, J. Hopkinson, and T. T. P. B. Warren observed that the magnetic power of nickel is enfeebled or destroyed by the addition of copper. The last-named observed that alloys with over 33·78 per cent. of copper are non-magnetic; and G. Reichard noted that the cupronickels are non-magnetic. According to E. H. Williams, although copper is only weakly magnetic, it requires 0·8 to 0·9 per cent. of nickel to neutralize its diamagnetic effect, and 56 per cent. of nickel is required before the alloy shows ferromagnetic properties at ordinary temp. The magnetic properties were studied by K. Honda, E. H. Williams, A. Kussmann and B. Scharnoff, M. N. Michejeff, E. C. Stoner, G. W. Elmen, P. Chévenard, D. R. Inglis, A. Krupkowsky, E. M. Deloraine, A. Sacklowsky, R. Gans and A. Fonseca, A. Fonseca, W. Dehlinger, and A. E. Kennelly; and the non-magnetic alloys, by J. Cournot. W. Guertler and G. Tammann found that an alloy with 40 per cent. of copper has but a feeble action on a magnetic needle at room temp., and alloys with less nickel have no perceptible action on the needle. Their observations on the effect of composition on the temp. at which the magnetization disappears are summarized in Fig. 116, and B. V. Hill observed that the transformation with alloys of different composition, occurs at

Copper		0	4	8	20	40 per cent.
Transition temp.	Hard alloy	355°	310°	280°	155°	—100°
	Annealed alloy	340°	295°	265°	140°	—

The temp. at which monel metal loses its magnetic property is near that of boiling water. B. V. Hill's observations on the intensity of magnetization at different temp. with alloys containing 0, 4, 8, and 20 per cent. of copper are summarized in Fig. 116, and the effect of magnetic fields of 13 and 63 c.g.s. units with the 8 per cent. copper alloy for hard-drawn and annealed alloy, in Fig. 117. The dotted lines refer to the annealed alloy, and the continuous lines to the hard-drawn alloys. The results show that the transition from the magnetic to the non-magnetic state, or *vice versa*, is not abrupt, but gradual. B. V. Hill explained the phenomenon by assuming that, on cooling, as soon as a position of the β- or non-magnetic nickel has been transformed into the α- or magnetic nickel, it at once dissolves in the remaining β-metal and so lowers the transformation temp. requiring a further fall of temp. before the transformation can continue.

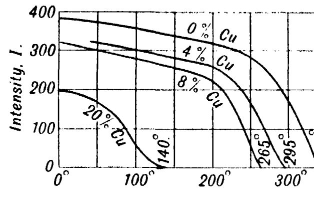


FIG. 116.—The Effect of Temperature on the Intensity of Magnetization of Copper-Nickel Alloys.

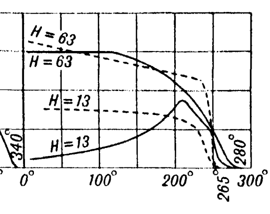


FIG. 117.—The Effect of the Field Strength on the Intensity of Magnetization of the 8 per cent. Copper Alloys at different Temperature.

R. Gans and A. Fonseca measured the magnetic susceptibility of the alloys and found that it varies at 15° from $0{\cdot}038\times10^{-6}$ with 20·3 per cent. of nickel, to $4{\cdot}565\times10^{-6}$ with 60 per cent. of nickel. There is a break with between 45 and 50 per cent. nickel. The magnetization of monel metal was studied by A. Schulze, and A. Kussmann. The effect of the change at the Curie point on the catalytic action of the alloy in the reaction $2CO=CO_2+C$ was studied by J. A. Hedvall.

According to C. W. Burrows, the magnetic induction of monel metal is dependent on the heat treatment. The lowest permeability in monel metal is obtained by heating it to 700°, cooling to 180°, and finally quenching in brine at −9°. The highest permeability is obtained by annealing the metal at 700°. The magnetic induction of four samples, A hot rolled rod) B (hot-rolled sheet), C (cast rod), and D (cast rod), of monel metal—quenched or cast (continuous lines) and annealed (dotted lines)—is summarized in Fig. 118. The influence of hot working is shown by comparing the curves for the cast and annealed material. The cast and annealed metal shows the lowest induction, and the hot rolled and annealed sheet metal shows the highest induction. In general, hot working increases the magnetic softness of monel metal, the cast metal is the hardest magnetically, and the sheet which has received the most hot working is the softest magnetically. Cold working alters the magnetic properties of monel metal, and for large magnetizing forces the changes are similar in nature and magnitude to those produced in the magnetic properties of steel. A 25 cm. monel metal bar was hammered until it showed an increase of 2½ per cent., and the change in permeability between the original and the hammered bar was:

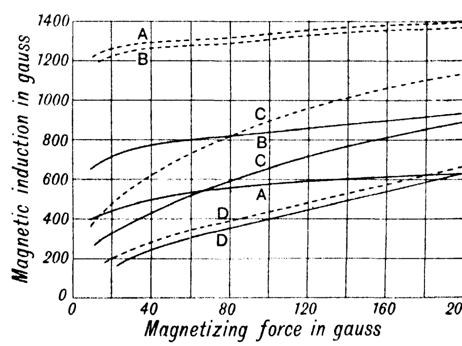


FIG. 118.—Magnetic Induction of Monel Metal.

Magnetizing force . .	1	2·5	5	10	25	50	100	200
Change in permeability	+100	−17	−27	−29	−28	−28	−14	−12 per cent.

W. Kohl measured the saturation value, $4\pi l$, of the magnetism of some copper-nickel alloys with an applied magnetizing force H in c.g.s. units. The values of $4\pi l$ for the prepared alloys were :

Copper	0	5	10	15	20	25	30	35	40 per cent.
H 50	1550	1725	1615	1730	1720	1160	310	45	25
H 300	4630	4155	3560	2985	2480	1475	545	160	120
H 800	5560	4965	4150	3485	2815	1660	760	400	325

The following is a selection from the results for the alloy heated for 4 to 6 hrs. at a temp. $\theta°$, and then quenched :

Copper	0	5	10	15	20	25 per cent.
(θ=400°)H 50	2200	1910	1615	1530	1685	1160
(θ=400°)H 300	5335	4505	3745	3135	2480	1475
(θ=400°)H 800	6040	5060	4300	3720	2815	1660
(θ=550°)H 50	3585	2760	2040	1790	1685	1290
(θ=550°)H 300	6150	5060	4300	3485	2815	1675
(θ=550°)H 800	6465	5360	4560	3820	3000	1805
(θ=650°)H 50	3190	2780	2465	2105	1850	1150
(θ=650°)H 300	6010	4910	4375	3690	2925	1710
(θ=650°)H 800	6265	5320	4615	3890	3020	1785
(θ=750°)H 50	4570	3150	3000	2820	2065	1490
(θ=750°)H 300	7225	6040	5210	4405	3370	2060
(θ=750°)H 800	7600	6430	5615	4665	3650	2265
(θ=950°)H 50	4375	3115	2835	2380	2000	1485
(θ=950°)H 300	7200	5650	4930	4170	3130	2095
(θ=950°)H 800	7590	6210	5335	4480	3370	2175
(θ=1250°)H 50	4885	3260	2650	2570	1890	1380
(θ=1250°)H 300	7280	5690	4390	3595	2635	1840
(θ=1250°)H 800	7425	6040	4580	3690	2720	1885

According to E. H. Williams, alloys with from 1 to 30 per cent. of nickel are mostly paramagnetic, and do not obey any known law of paramagnetism with respect to temp., for as the temp. is increased, the magnetic susceptibility first increases and then decreases, the maximum occurring in the neighbourhood of the Curie point for nickel. The susceptibility of alloys with over 30 per cent. of nickel decreases with a rise of temp. for temp. above 20°. Observations were also made by W. H. Ross.

O. E. Buckley and L. W. McKeehan found that when under tension permalloy with less than 81 per cent. nickel is more easily magnetized and has less hysteresis ; and permalloy with over 81 per cent. of nickel is more difficult to magnetize and has more hysteresis ; whilst permalloy with 80 per cent. of nickel is indifferent to tension. S. R. Williams examined the magnetostriction of hot and cold rolled rods of monel metal. If a constant magnetizing field of 1000 gauss is left impressed on a monel metal rod, the rod continues to shorten. This after-effect is 4 to 5 times greater than the change in length due to variations in the strength of the imposed magnetic field. A. Schulze observed no magnetostriction with hard monel metal for fields of 150 gauss for 20 hrs. and 500 gauss for 1 hr. ; and a contraction with soft monel metal. The contraction is the greater the higher is the proportion of contained nickel. A. W. Smith and J. Dillinger measured the combined effect of tension and of a longitudinal magnetic field on the thermoelectric force (*q.v.*) of a permalloy and copper couple. In permalloy with a high proportion of nickel, say 84 per cent., tension decreases the intensity of magnetization for low magnetic fields, but it increases the magnetostriction contraction, and the change of thermal e.m.f. ; in alloys with a low proportion of nickel, say 78 per cent., tension increases the intensity of magnetization for low magnetic fields, but it decreases the magnetostrictive expansion and the change of thermal e.m.f. L. W. McKeehan and P. P. Cioffi observed that the magnetostriction of permalloy with over 81 per cent. of nickel is a contraction like nickel and an expansion like iron with less than 81 per cent. Tension increases the magnetostrictive contraction and diminishes the expansion. There is a reversal of sign with about 80 per cent. nickel. Observations

were made by A. Schulze, and P. Chévenard. R. Forrer studied the magnetic moment; and W. Sucksmith, the gyromagnetic effect; A. Kussmann and B. Scharnoff observed no relation between the coercive force and hardness.

E. Bergner studied the solubility of hydrogen in the alloys; W. Baukloh and H. Kayser, and G. Wagner and co-workers, the copper-nickel alloys as hydrogenation catalysts. According to F. A. Geitner, a copper-nickel alloy tarnished in air more quickly than German silver. C. E. Guillaume observed that the alloys he examined did not tarnish in air; and those examined by K. Feussner and St. Lindeck did not acquire a noticeable tarnish after being heated over 300°. Actually, W. T. Griffiths stated that the resistance of the alloy to atm. attack increases with the proportion of nickel so that a polished surface of the 40 to 45 per cent. nickel alloy is dulled only after a long exposure to atmospheric influences. W. H. J. Vernon observed that the tendency of the alloys to fogging in atm. air is solely dependent on the proportion of nickel—the copper is inert—*vide* nickel. Monel metal resists oxidation fairly well up to about 750°. N. B. Pilling and R. E. Bedworth studied the oxidation of these alloys at a high temp., and found after 1 hr.'s heating at approximately the temp. named, the increases in weight, w grms. per sq. cm., were as follow:

Nickel (per cent.)	750°	800°	850°	900°	950°	1000°
10	0·0054	0·0073	0·0117	0·0168	0·0237	—
15	0·0049	0·0080	0·0118	0·0156	0·0266	—
20	0·0059	0·0087	0·0121	0·0172	0·0245	—
30	—	0·0087	0·0115	0·0181	0·0190	—
40	—	—	0·0055	0·0129	0·0192	0·0360
50	—	—	0·0043	0·0103	0·0141	0·0364
60	—	—	0·0013	0·0058	0·0154	0·0309
70	—	—	0·0012	0·0022	0·0027	0·0043
85	—	—	—	0·0016	0·0024	0·0031
90	—	—	—	0·0012	0·0040	0·0027
95	—	—	—	0·0012	0·0017	0·0021

The alloys with 40 to 70 per cent. of nickel do not follow the same "law" of oxidation as the other alloys. The alloys with up to 40 per cent. of nickel behave very like copper, but above this proportion of nickel, the rate of oxidation falls off in a marked way. The subject was also studied by T. H. Chilton and W. R. Huey, G. M. Enos, F. A. Fahrenwald, W. H. Finkeldey, A. C. Hanson, J. C. Hudson, F. Orme, S. B. Redfield, J. Ruhrmann, P. Siebe and C. Busse, G. Tammann and H. Bredemeier, and J. R. Tanner and G. F. Smart. C. Künzel stated that the alloys with over 10 per cent. of nickel are very prone to absorb oxygen when they are melted. N. P. Allen and A. C. Street studied the effect of occluded hydrogen and oxygen on the mechanical properties. C. E. Guillaume observed that water vapour attacks the nickel alloys feebly; and G. and J. Weir recommended monel metal for use with superheated or wet steam. W. G. Whitman and R. P. Russell studied the action of oxygen dissolved in water on monel metal. C. Diegel stated that sea-water attacks the 20 and 40 per cent. nickel alloys slightly, and still less so if the alloy be in contact with other "sacrificial" metals like iron. J. A. N. Friend and co-workers, and J. McNeil examined the effect of sea-water. J. F. Saffy found that an alloy with 29 per cent. of copper broke with a deep crack after being 2 weeks in steam and bent at 180°; after 7 weeks in steam, it broke at an angle of 90° to 120°. W. R. E. Hodgkinson and A. H. Coote said that an ammoniacal soln. of hydrogen dioxide has less action on the nickel-copper alloys than it has on copper alone; and soln. of ammonium nitrate have less action than when they are mixed with hydrogen dioxide, or ammonia.

Very dil. soln. of the mineral acids do not attack the higher nickel alloys very rapidly, but an increased concentration leads to a more rapid attack for alloys with less than 50 per cent. of nickel, and the attack is greatest with nitric acid, and least with sulphuric acid. The corrosion of monel metal in acids, etc., was studied by M. G. Binek, J. Desmurs, G. A. Drysdale, H. J. French, G. Grube and A. Jedele,

J. C. Hudson, A. Jäschke, C. M. Johnson, J. W. McMyn and V. Edge, F. A. Rohrman, E. Rabald, F. Renaud, and G. Weissenberger and L. Piatti. R. Irmann observed that the attack of sulphuric acid in mgrms. per sq. cm. of the surface of copper-nickel alloys is as follows:

Copper .	0	10·6	25·0	42·6	47·8	59·4	100 per cent.
Loss .	33·00	31·03	14·77	3·98	0·39	2·16	2·89

The results are plotted in Fig. 119. The maximum resistance to attack occurs with about 50 per cent. of copper. D. F. McFarland and O. E. Harder obtained for the corrosion of the alloys the results in Table V with normal nitric, hydrochloric, and sulphuric acids, normal soln. of sodium chloride and hydroxide, ammonium hydroxide and fatty acids, expressed in terms of the loss in weight in mgrms. per sq. in. per week. M. Waehlert found the losses in mgrms. per sq. cm.—during the time in hours indicated in brackets—with nitric and sulphuric acids, indicated in Table VI. R. J. McKay said the passivity which is produced when nickel is exposed to highly corrosive influences is evident in the higher nickel alloys like monel metal which is fairly resistant to acid corrosion. It resists 10 per cent. sulphuric acid rather better than does nickel, yet in 10 per cent. nitric acid, the

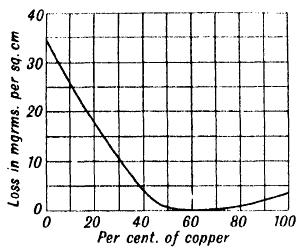


FIG. 119.—The Action of Acid on Copper-Nickel Alloys.

TABLE V.—THE CORROSION OF THE NICKEL-COPPER ALLOYS.

Nickel (per cent.)	NaCl	HCl	H_2SO_4	HNO_3	NaOH	NH_4OH	Fatty acids
0 .	5·08	45·0	31·00	30·80	15·00	41·80	8·90
9·29 .	4·18	20·0	19·50	41·40	5·90	46·40	—
18·73 .	1·60	34·2	18·40	27·70	0·00	46·30	5·80
28·35 .	1·68	29·3	19·00	25·10	0·00	37·30	—
38·10 .	2·35	26·7	17·00	21·40	0·16	18·80	2·90
48·00 .	2·37	21·2	15·10	11·40	0·16	0·00	—
58·06 .	0·78	7·1	19·30	22·40	1·10	2·20	—
68·30 .	1·71	23·0	17·40	11·40	0·13	33·60	4·00
78·79 .	1·71	16·5	11·70	14·80	2·60	15·20	—
89·26 .	1·13	18·2	16·40	11·60	0·32	0·97	—
100·00 .	0·00	207·0	19·40	2270·00	18·70	15·90	—

TABLE VI.—THE ACTION OF ACIDS ON THE NICKEL-COPPER ALLOYS.

Conc. of acid (per cent.)		Per cent. of copper in alloy							
		90	80	70	60	50	40	30	20
HNO_3	1(48) .	0·60	0·42	0·36	0·42	0·60	0·68	—	0·68
	5(24) .	2·75	3·35	2·10	2·10	0·95	0·48	—	0·10
	10(24) .	44·30	13·30	3·65	4·00	1·78	1·30	—	0·75
	20(24) .	49·70	16·40	4·60	1·20	0·51	0·34	—	0·34
	30(24) .	422·50	92·50	16·30	1·17	0·34	0·34	—	0·68
	50(24) .	—	—	693·50	46·20	19·50	7·98	—	27·90
H_2SO_4	1(72) .	0·01	—	0·25	—	—	—	0·51	—
	5(24) .	0·17	0·17	0·17	0·08	—	0·17	0·25	0·34
	10(24) .	0·59	0·85	0·42	0·60	1·10	0·43	0·25	0·43
	20(24) .	—	—	—	0·07	—	0·07	0·08	—
	30(24) .	—	—	—	0·07	—	—	—	—
	50(24) .	—	—	—	0·07	—	—	—	—

nickel becomes more passive and is less rapidly attacked. The presence of an unstable, strong oxidizing agent favours the attack by strong acids. Monel may resist a strong oxidizing agent alone—*e.g.* liquid chlorine, or alkaline bleaching agents like peroxide, or hypochlorites; and it may also resist the action of the acid alone, but a mixture of the two attacks the metal fairly quickly. H. Endo and H. Sekiguchi, J. W. McMyn and V. Edge, and G. N. Quam studied the action of hypochlorites. E. S. Sperry found that an aq. soln. of chlorine water dissolves the powdered alloy. The Nya Akkumulator Aktiebolaget found that the alloys with 60 and 70 per cent. of nickel resist very well the anodic attack during the electrolysis of soln. of the alkalies.

B. C. Banerji and N. R. Dhar observed that with a 50 : 50 alloy, the action of 20 per cent. nitric acid was accelerated by the presence of ferrous sulphate or of ferric nitrate or chloride. According to W. Rohn, 10 per cent. hydrochloric acid dissolves 0·052 grm. per sq. dm. from constantan in 24 hrs. in the cold, and 0·11 grm. per sq. dm. in an hour when heated. The corresponding data for the annealed constantan are respectively 0·073 and 0·29 grm.; for ordinary monel metal, 0·06 and 0·17 grm.; and for annealed monel metal, 0·04 and 0·23 grm. With 10 per cent. nitric acid, the data are respectively 0·06 and 19·4 grms. for constantan; 0·24 and 7·6 for annealed constantan; 0·044 and 1·2 grms. for ordinary monel metal, and 0·02 and 0·73 grm. for annealed monel metal. For 10 per cent. sulphuric acid, the data are respectively 0·005 and 0·003 grm. for ordinary constantan; 0·01 and 0·012 grm. for annealed constantan; 0·016 and 0·008 grm. for ordinary monel metal; and 0·012 and 0·004 grm. for annealed monel metal. For 10 per cent. acetic acid, the data are respectively 0·004 and 0·002 grm. for ordinary constantan; 0·002 and 0·004 grm. for annealed constantan; 0·002 and 0·006 grm. for ordinary monel metal; and 0·004 grm. for annealed monel metal. For 10 per cent. phosphoric acid, the data are respectively 0·004 and 0·01 grm. for ordinary constantan; 0·002 and 0·008 grm. for annealed constantan; 0·006 and 0·016 grm. for ordinary monel metal; and 0·002 and 0·01 grm. for annealed monel metal. J. I. Crabtree and G. E. Matthews observed that 5 per cent. sulphuric acid dissolves monel metal at the rate of 0·69 grm. per 100 sq. in. per day; and with 5 per cent. nitric acid, the loss is 0·45 grm. per 100 sq. cm. per day. S. Croasdale found that after six weeks' immersion in 10 per cent. sulphuric acid, 10 per cent. copper sulphate, a mixture with 10 per cent. each of sulphuric acid and copper sulphate, monel metal lost 2·81, 1·99, and 4·88 per cent. respectively. O. B. J. Frazer and co-workers observed that the corrosion of monel metal in 5 per cent. sulphuric acid varies directly with the concentration of the dissolved oxygen, and it reaches a maximum when the soln. is saturated with oxygen. A. F. Crosse dropped the acidic water—0·40 per cent. free H_2SO_4—continuously for six days on pieces of monel metal and iron; the latter was soon corroded, but the monel metal remained unaffected though stained by the deposit from evaporated water. After two days' immersion in 3·5 per cent. sulphuric acid, a monel metal rod had lost only 0·04 grm. of copper from an exposed surface of 40 sq. mm., whereas with iron, a sat. soln. of ferrous sulphate was formed. Hence, it would take 2000 days to dissolve a thickness of one-thousandth of an inch of monel metal. I. P. Podolsky and N. M. Zarubin found that sulphur vapour attacks the copper faster than the nickel. J. S. Vanick studied the attack by hot ammonia gas; L. Pessel, and P. D. Merica, the attack by sulphurous acid. J. I. Crabtree and G. E. Matthews found that hydroquinone or pyrogallol developing baths, and sodium thiosulphate in hypo-fixing baths do not attack monel metal very much; nicolene is rather more attacked. F. Clarkson and H. C. Hetherington observed that monel metal is but slightly affected by conc. phosphoric acid at ordinary temp.; and V. K. Perschke and co-workers observed that 80 per cent. copper alloys resisted the action of conc. phosphoric acid at 150° very well. E. Maass and W. Wiederholt found that the attack by dry salts decreases in this order—magnesium chloride, carnellite, Hartsalz, potassium chloride, sodium chloride, and magnesium sulphate. H. S. Rawdon and E. C. Groesbeck found

that for nickel-copper alloys the losses in N-NaCl soln. expressed in milligrams per sq. dm. per 24 hrs. were :

Ni	0	28·9	44·6	70·0	98·9 per cent.
Loss . . .	9·0	3·50	1·00	0·8	9·20

V. O. Homerberg and J. P. Walstead studied the resistance to wear of the nitrogenized alloy. P. Parrish studied the corrosion of monel metal by ammonium salts ; M. Donauer, fruit juices ; E. M. Mrak and W. V. Cruess, fruit juices with sulphur dioxide ; and M. P. Balfe and H. Phillips, by tan liquors.

The alloys resist the attack by certain acid fruit juices and other organic acids. In virtue of the fact that the alloys contain only one phase or solid soln., they have the advantage of being uniformly attacked without localized corrosion or pitting, which lead most rapidly to structural breakdowns. G. and J. Weir recommend monel metal where the action of alum, aluminium sulphate, alkaline soap, ammonia, benzoic acid, boric acid, butyric acid, calcium sulphate, calcium chloride, carbolic acid, chlorine, formic acid, hydrocyanic acid, hydrofluoric acid, hydrogen, lactic acid, lime, malic acid, mercury, oleic acid, oxygen, palmitic acid, cold and dil. phosphoric acid, cold picric acid, potassium hydroxide, salicyclic acid, sodium hydroxide, sodium thiosulphate, stearic acid, sulphur dioxide, tartaric acid, and water—fresh and salt—is concerned. It is not recommended for ammonium nitrate in sat. soln., chromic acid, copper sulphate, mercuric chloride, nitric acid, perchloric acid, phosphoric acid—hot soln., picric acid—hot soln. or sulphurous acid. O. Bauer and H. Arndt studied the action of soap soln., and bleaching and washing fluids ; and F. H. Rhodes and co-workers, the attack by phenols. R. J. McKay and co-workers, and W. A. Wesley and co-workers noted the action of hot, aerated milk. A. Gansser reported how well monel metal resisted the action of tanning liquors ; and C. Fichandler, boiling linseed oil. K. Yoshikawa studied the action of thiophen on the alloy used as a catalyst.

W. Guertler and T. Liepus observed that the 1 : 1-alloy of nickel and copper is attacked in 8 hrs. by 10 and 50 per cent. nitric acid ; 10 and 36 per cent. hydrochloric acid ; aqua regia ; 10 per cent. sulphuric acid, and 20 per cent. sulphuric acid sat. with sodium sulphate ; carbon dioxide and air ; acetic, citric, and tartaric acids ; 10, 50, and 70 per cent. aq. ammonia ; 10 and 50 per cent. sodium sulphide, and 4 per cent. sodium sulphide mixed with 8 per cent. of alkali ; chlorine water ; sea-water ; sea-water and air ; rain-water and air ; and a soln. of magnesium chloride. Whilst a 50 per cent. soln. of sodium hydroxide attacked the alloy in 8 hrs.' action, a 10 per cent. had no action in 48 hrs., and a soln. of soda-lye and hydrogen dioxide had no action in 48 hrs. The alloy decomposed a 1 : 500-soln. of mercuric chloride. R. Adan discussed the action of soda-lye on copper-nickel alloys. According to A. F. Crosse, 0·13 grm. of copper was dissolved from an exposed surface of 112 sq. cm. of monel metal in 5 days by a 0·12 per cent. soln. of potassium cyanide under conditions where iron remained unaffected. Washers of monel metal, weighing 39·88 grms., were immersed for 5 days in a 0·05 per cent. soln. of free hydrocyanic acid, and lost 0·01 grm. of copper per 30 sq. cms. of surface. Iron washers under similar conditions lost 0·05 grm. in 40 grms. The corrodibility of the nickel-copper alloys was studied by M. Waehlert, E. Maass and W. Wiederholt, R. Irmann, P. D. Merica, J. Arnott, P. Chévenard, R. J. McKay, F. Orme, G. Weissenberger and L. Piatti, W. H. J. Vernon, W. R. Barclay, J. F. Haerry, and J. L. Everhart. D. J. McAdam, and M. G. Binek studied the corrosion of monel metal under cyclic stresses—*vide supra*, corrosion fatigue. W. Meissner, and K. L. Meissner studied the **copper-nickel-bismuth alloys.** M. Ballay and A. le Thomas, E. Crepaz, C. H. M. Jenkins and E. E. Bucknall, B. W. Gouser and L. R. van Wert, and M. G. Corson studied the **nickel-copper-silicon alloys.**

W. A. Lampadius [2] prepared **nickel-silver alloys.** He noticed that combination takes place with difficulty and imperfectly to form malleable alloys. E. Pannain also noted that alloys are formed with difficulty, but in the presence of a third

metal alloy takes place more readily; F. Ducelliez found a difficulty in preparing homogeneous alloys, and stated that the products are mixtures of the components; and E. Vigouroux added that no compounds are formed. Alloys were also made by G. J. Fowler and P. J. Hartog; P. Benvemuti prepared the alloys electrolytically. W. A. Ross observed that molten nickel can dissolve much silver, but molten silver does not take up much nickel. G. Barruel added that the alloy of silver with 0·05 per cent. of nickel is very hard. J. R. Townsend and C. H. Greenall studied the fatigue test. G. Tammann and W. Oelsen gave for the solubility, S per cent., of nickel in silver, $\log S = -1991T^{-1} + 0·688$, and found:

	962°	860°	740°	600°	510°	400°
S . . .	0·122	0·084	0·051	0·026	0·018	0·012

and by extrapolation S, at 20°, is $0·0_{6}78$ per cent. of nickel. S. Tanaka and C. Matano studied the diffusion in the silver-nickel system. G. J. Petrenko said that silver is soluble in nickel to the extent of 0·4 per cent., and the m.p. is thereby lowered 20°—*vide* Fig. 120. On solidification, homogeneous solid soln. separate out. With over 4 per cent. of silver, the metals form two layers. The m.p. of silver is not affected by nickel so that nickel is insoluble in silver at the m.p. of

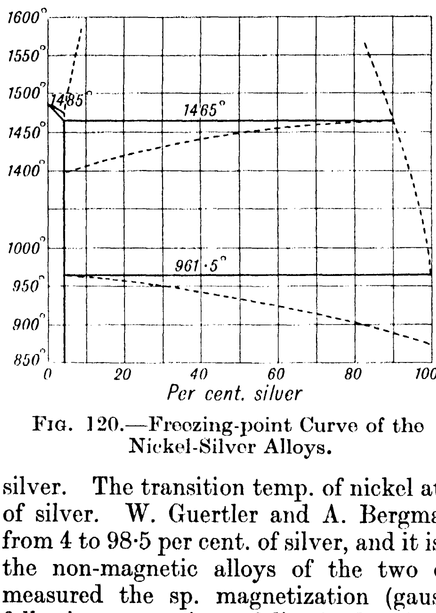


FIG. 120.—Freezing-point Curve of the Nickel-Silver Alloys.

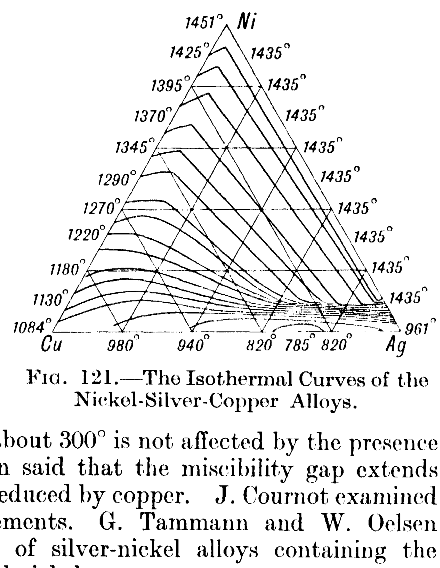


FIG. 121.—The Isothermal Curves of the Nickel-Silver-Copper Alloys.

silver. The transition temp. of nickel at about 300° is not affected by the presence of silver. W. Guertler and A. Bergmann said that the miscibility gap extends from 4 to 98·5 per cent. of silver, and it is reduced by copper. J. Cournot examined the non-magnetic alloys of the two elements. G. Tammann and W. Oelsen measured the sp. magnetization (gauss) of silver-nickel alloys containing the following proportions of dissolved and total nickel:

		962°	860°	740°	640°	530°	400°	200°
Dissolved Ni . . .		0·122	0·084	0·051	0·032	0·020	0·012	0·012
Gauss	0·0501 per cent. Ni	−0·255	−0·129	−0·074	5·75	14·9	19·6	19·8
	0·147 per cent. Ni	12·51	37·9	54·4	63·7	72·5	76·3	76·3
	0·242 per cent. Ni	61·8	93·4	110·9	118·1	126·9	129·8	129·2

E. Vigouroux observed the e.m.f. of the alloys in acids, and found that the e.m.f. in a normal soln. of silver sulphate shows that the alloys are mixtures; and that a solid soln. of silver in nickel may exist. N. F. Mott studied the effect of magnetization on the resistance. A. Renaud, and L. Jordan and co-workers studied the resistance of the alloys to tarnish. P. de Cesaris' observations on the f.p. of the **nickel-silver-copper** alloys are summarized by the isothermal f.p. curves, Fig. 121. Observations on the ternary system were also made by W. Guertler and A. Bergmann, and H. Pfister and P. Wiest.

W. A. Lampadius[3] prepared **nickel-gold alloys**; he said that the two metals readily unite to form a yellowish-white, hard, very malleable alloy

which can take a high polish, and which has a magnetic power as great as that of nickel; W. Jones prepared some alloys, and Richter and Co. observed that with higher proportions of nickel, the alloys are white in colour. K. Fischbeck, and A. Jedele studied the diffusion of gold and nickel. E. Jänecke stated that a eutectic occurs at 950°; and P. de Cesaris, at 955°. The latter added that the limits of miscibility lie at 8 per cent. of nickel in gold, and 20 per cent. of gold in nickel. M. Levin found that the f.p. curve, Fig. 122, gives no evidence of the formation of compounds. There is an interval of crystal-

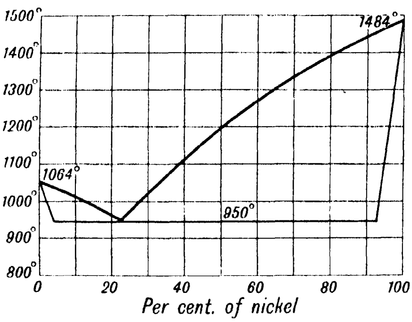


FIG. 122.—Freezing-point Curve of the Nickel-Gold Alloys.

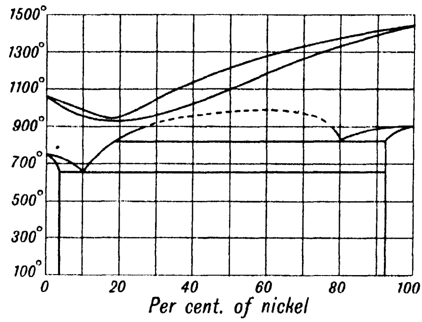


FIG. 123.—Freezing-point Curve of the Nickel-Gold Alloys.

lization with alloys containing 5 to 20 and 50 to 70 per cent. of nickel; and the eutectic occurs at 950° and over 20 per cent. of nickel. There are two series of solid soln. There are two constituents in alloys with from 20 to 90 per cent. of nickel one of which is rapidly attacked by nitric acid, and the other slowly. Alloys with 5 to 10 per cent. of nickel are homogeneous. The transformation temp. of the alloys is very near that for pure nickel, 323°, showing that this temp. is not affected by the proportion of gold in the alloy. According to W. Fränkel and

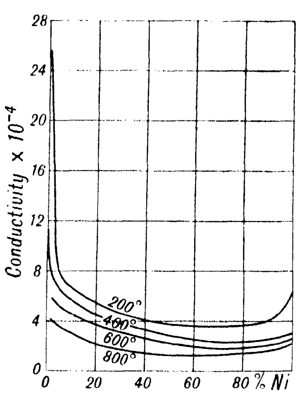


FIG. 124.—The Electrical Conductivities of the Nickel-Gold Alloys.

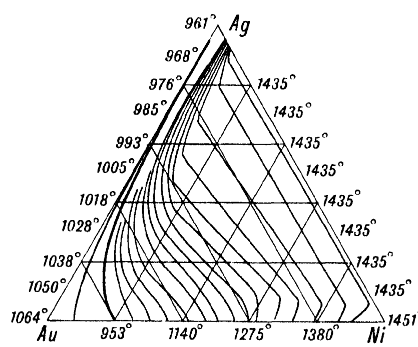


FIG. 125.—The Isothermal Curves of the Nickel-Gold-Silver Alloys.

A. Stern, the crystallization temp. of the gold-nickel alloys lies on a continuous curve with a minimum at 950° for alloys with 15 to 20 per cent. of nickel. A continuous series of solid soln. is thus formed so that the 20 and 40 per cent. alloys are homogeneous. The former corresponds with the supposed minimum of M. Levin, and P. de Cesaris. E. Kordes, N. S. Kurnakoff and A. N. Achnasaroff, and A. Renaud discussed this subject.

A. Westgren and W. Ekman discussed the lattice structure. H. Hafner obtained similar results, Fig. 123, and the changes in the solid soln. are represented by the

curves in the same diagram. W. Heike and H. Kessner also found that these alloys suffer marked changes in structures when heated for prolonged periods between 100° and 550°. A soln. of potassium sulphide is a good etching liquid. The specific electrical conductivities of the nickel-gold alloys were measured by G. Grube and F. Vaupel, and the results are summarized in Fig. 124; and the effect of pressure, by J. O. Linde; and the thermoelectric force, by G. Borelius and co-workers. The alloys were studied by L. Nowack, and E. M. Wise. E. Vogt and H. Krüger investigated the magnetic properties of the alloys; N. F. Mott, the effect of magnetization on the conductivity; and W. H. Keesom and C. J. Matthijs, the thermoelectric force between −270·5° and −255·5°. J. Cournot examined the non-magnetic alloys. H. Seltz, P. de Cesaris, and E. M. Wise studied the **nickel-gold-copper alloys**; and P. de Cesaris' observations on the f.p. of the **nickel-gold-silver alloys** are summarized by the isothermal f.p. curves, Fig. 125. The alloy *proplatinum* contains Ni, 72·00; Ag, 23·57; Au, 0·71; Bi, 3·72. N. Parravano studied the quaternary **copper-silver-gold-nickel alloys.**

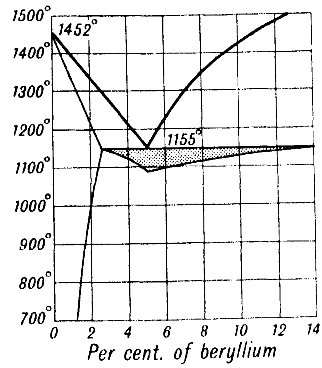


FIG. 126.—The Freezing-point Curve of the Binary System: Ni–Be.

H. Moissan[4] prepared brittle **calcium-nickel alloys** by direct union of the elements; and N. Tarugi, by heating a nickel salt with calcium carbide. The alloys are decomposed by water. P. H. Brace, N. C. Breese, L. Misch, and O. S. Duffendack and D. W. Randolph utilized a **nickel-barium alloy** with 5 to 25 per cent. of barium for radio-valve filaments, and sparking electrodes. H. Boving described the preparation of filaments of nickel alloyed with alkaline earth metals. G. Masing and O. Dahl, and W. Hessenbruch studied the **nickel-beryllium alloys.** The f.p. of the alloys are:

Beryllium .	6·16	11·72	16·75	21·33	29·34	36·13	41·94 per cent.
Freezing-point	1406°	1344°	1293°	1242°	1215°	1348°	1435°

The corresponding portion of the equilibrium diagram is plotted in Fig. 126. They also studied the microstructure of these alloys. The effect of annealing on the hardness of the alloys with 3 per cent. of beryllium, quenched from 1100°, is summarized in Fig. 127. I. Fetchenko-Tchopivsky studied the cementation of nickel with beryllium; and C. Matano, the effect of temp. on the diffusion. L. M. Jackson discussed the improvement in the hardness of nickel, and of nickel-copper alloys, when beryllium is present. According to G. Masing and O. Dahl, the mechanical properties, expressed in kilograms per sq. mm. of alloys quenched and aged for $6\frac{1}{2}$ hrs. at 500°, are:

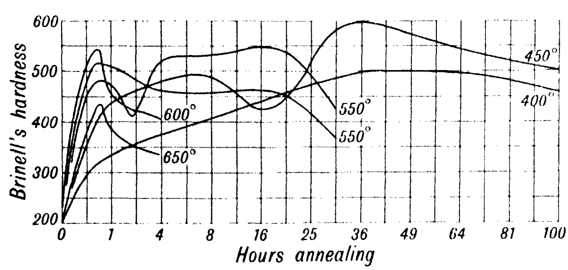


FIG. 127.—The Effect of Annealing on the Hardness of Nickel-Beryllium Alloy.

Beryllium (per cent.)		Hardness	Elastic limit	Proportional limit	Ultimate fracture	Elongation (per cent.)	Elastic modulus
0 . . .		60	2	—	40·0	45	20,500
2·5	quenched .	162	15·6	24·4	57·4	16·8	18,427
	aged .	412	31·8	—	107·7	2·0	20,089
3·0	quenched .	193	25·2	43·8	71·4	9·0	18,502
	aged .	531	111·6	—	132·0	0	20,022

W. Kroll observed :

Ni : Be		Tensile strength	Elongation (per cent.)	Reduction area (per cent.)	Hardness Brinell's
5 : 1	quenched	13·0	7	52·0	425
	annealed	1·82	3	3·0	610
15 : 1	quenched	130	7	43·0	360
	annealed	—	2	—	588
36 : 1	quenched	59	27	46·0	150
	annealed	112	5	14·0	295

W. Hessenbruch, and H. A. Sloman studied the subject. The electrical resistance, R ohms, and the magnetic properties are :

Beryllium	0·0	0·35	0·70	1·41	2·40 per cent.
Coercive force	1·6	2·25	2·50	2·60	4·10
Remanence	3200	8100	6800	6700	8200
Permeability Max.	2200	1850	1880	1100	920
Permeability H_{120}	1600	1570	1700	1370	1350
R	$0{\cdot}0_4 10$	$0{\cdot}0_4 164$	$0{\cdot}0_4 24$	$0{\cdot}0_4 40$	$0{\cdot}0_4 57$

A. Krussmann studied the magnetic properties of the alloys. The corrosive action of acids expressed as a loss in mgrms. per sq. cm., found by G. Masing and O. Dahl, is as follows:

Beryllium	0	1(Mn)	1·5	2·0	2·5	3·0 per cent.
HNO_3 (3 per cent.)	5·4	6·5	12·6	12·1	54·0	31·4
HCl (3 per cent.)	1·32	2·8	2·56	3·1	3·1	2·2

M. Ballay, M. G. Corson, and G. Masing and W. Pocher examined some **copper-nickel-beryllium alloys.**

J. Parkinson [5] could not prepare **nickel-magnesium alloys** directly. A. Coehn obtained alloys with up to 10 per cent. of magnesium by the electrolysis of a mixed soln. of nickel and magnesium salts. The proportion of magnesium is greater, the higher is the temp. of electrolysis and the greater is the ratio Mg : Ni in the electrolyte. T. Fleitmann obtained the alloys by melting the metals together, or by the simultaneous reduction of the oxides. The 0·5 per cent. magnesium alloy obtained in this way can be rolled or hammered, and it retains its ductility when cold. The preparation of the alloys was studied by W. V. Veazey. G. Voss found the metals to be completely miscible in the fused state. The f.p. curve, Fig. 128, shows a flattened portion, not a true maximum, at 1145° and 75 to 83 per cent. of nickel. This corresponds with the existence of **nickel hemimagneside,** Ni_2Mg, which appears in thin leaflets. The eutectic at 1082° and 89 per cent. of nickel has the phases : nickel and the hemimagneside ; the eutectic at 512° and 34 per cent. of nickel has the phases : magnesium and **nickel dimagneside,** $NiMg_2$. The break at 768° and 45 per cent. of nickel, corresponds with the formation of dimagneside by the breaking up of the hemimagneside. The magnetic transition temp. of nickel at 350° is not altered by the addition of up to 17 per cent. of magnesium, but with 17 to 45 per cent. of magnesium the transition occurs at 235°. Alloys with over 45 per cent. of magnesium are not magnetic at ordinary temp. The subject was studied by J. L. Haughton and R. J. M. Payne ; and W. Kroll investigated the hardness of

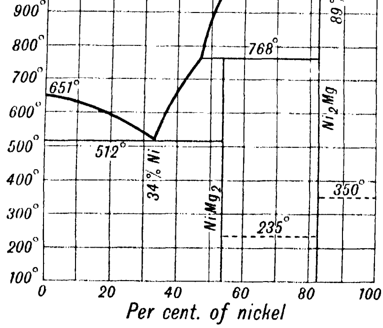


FIG. 128.—The Freezing-point Curve of Nickel-Magnesium Alloys.

the Ni-Mg-C alloys. G. Tammann and A. Rohmann found the heat capacity, c cals. per mol, for Ni_2Mg, to be :

	0°–100°	100°–200°	200°–300°	300°–400°	400°–500°
c . . .	1778·08	1856·01	1898·51	1933·93	1955·18

The hexagonal crystals of Ni_2Mg were found by T. Laves and H. Witte to have the parameters a=4·805 A., and c=15·77 A., and there are 8 molecules per unit cell. J. A. Gann studied the hardness of alloys with between 0·25 and 8 per cent. of nickel; P. Schübel, their sp. ht.; and J. Cournot examined the non-magnetic alloys of the two elements. A. Portevin and E. Pretet studied the rate of dissolution of the alloys in hydrochloric acid. F. C. Lea, W. Rosenhain and co-workers, W. Kroll, and S. L. Archbutt and co-workers studied the mechanical properties of these alloys, and of the **copper-nickel-magnesium alloys.**

A. F. Gehlen [6] obtained a brittle **nickel-zinc-alloy** by heating a mixture of nickel and zinc. The union is attended by the emission of a red-light, or, according to A. T. von Gersdorff, it is attended by combustion and explosion. T. Fleitmann obtained alloys by the simultaneous reduction of the oxides of the two metals, or by passing the vapour of zinc over nickel reduced from the oxide. Alloys were prepared by C. S. Cussen. According to G. Voss, compact nickel dissolves more rapidly in molten zinc than does powdered nickel. This may be due to films of air on the surfaces of the granules of the powder. V. E. Tafel melted the alloys under a layer of borax. E. P. Schoch and A. Hirsch, and H. C. Cocks observed that an alloy of zinc and nickel can be obtained by electrodeposition from soln. of zinc and nickel salts using a current density of 3 amps. per sq. dm. A bath containing more nickel than zinc yields an alloy containing far more zinc than nickel. The ratio of Zn : Ni in the alloy is from 4·5 to 14 times the ratio in the electrolyte according to the conc. of the electrolyte. The subject was studied by W. D. Treadwell, H. C. Cocks, F. Förster, S. Glasstone, A. S. Russell and co-workers, and G. Grube—*vide supra;* and the sp. gr. of the alloys, by K. Schmidt. C. T. Heycock and F. H. Neville observed that the f.p. of zinc is lowered by small additions of nickel. G. Voss investigated the alloys with up to 23 per cent. of nickel, and he found that with 14·5 to 23 per cent. of nickel, solid soln. of **nickel trizincide,** $NiZn_3$, and zinc separate out, but between 0° and 14·5 per cent. of nickel, the crystals of solid soln. are insoluble in those of zinc. The alloys are non-magnetic at room temp. V. E. Tafel observed a eutectic very close to the zinc end of the curve, and only 0·5° below the m.p. of zinc. The crystalline constituents observed were (i) pure zinc; (ii) solid soln. with 12·2 to 23·0 per cent. of nickel; (iii) the trizincide m.p. 876°; (iv) solid soln. with 39·7 to 45·8 per cent. of nickel which on cooling to about 645° break up into two other kinds of crystals, (v) and (vi). There are also crystals (vii) which separate from the molten mass, and react with it at 1025° to 1037° to form the solid soln. (iv). There are also solid soln. (viii) formed when alloys with over 45·8 per cent. of nickel are cooled to 780°. The nature of the solid soln. is not known; owing to the loss of zinc by volatilization, the diagram above 50 per cent. of nickel could not be completed except by extrapolation from a ternary model. K. Tamaru's, and K. Tamaru and A. Osawa's results are summarized in Fig. 129. The compound ZnNi forms a solid soln., δ, between 45·1 and 49·0 per cent. of nickel; the limit of the β-solid soln. extended to 37·5 per cent. of zinc at the eutectic temp. 872°; the range of the α-solid soln. narrowed down to 0 to 61·61 per cent. of nickel, and the solid soln. β and δ were formed respectively at 1043° and 804°. The eutectoid reaction $\beta=\alpha+\gamma$ occurs at 675° in the range of 24·4 to 45·1 per cent. of nickel. The α-solid soln. with $NiZn_3$ has a limiting conc. of 24·4 per cent. of nickel. W. Heike and co-workers also studied the structure of the nickel-zinc alloys. The subject was studied by K. Bornemann, W. Guertler, W. M. Peirce, V. Caglioti, P. Charrier, H. Hafner, W. Heike and co-workers, L. Guillet, and A. Westgren. A. Westgren, and W. Ekman studied the X-radiogram of **nickel pentitahenicosizincide,** Ni_5Zn_{21};

and also the relation between the crystal structure and the atomic properties of the nickel-zinc alloys. Nickel becomes more brittle when alloyed with zinc, and the trizincide is extremely brittle, and it gives a blue coloration with nitric acid. A. S. Russell and co-workers studied the compounds formed in mercury soln. T. J. Seebeck examined the magnetic polarization of the alloys.

E. Vigouroux and A. Bourbon observed that the alloys with less than 72·8 per cent. of nickel are non-magnetic. J. Cournot studied the non-magnetic alloys. When pulverized and subjected to the action of hydrochloric or acetic acid, the residues from mixtures containing up to 18·3 per cent. of nickel became progressively richer in this element and developed magnetic properties. The residues from mixtures containing over 18·3 per cent. nickel showed little variation in composition as the attack progressed. Alloys containing less than 18 per cent. of nickel on treatment with 1 per cent. nitric acid gave invariably a residue containing 18·6 per cent. of nickel, corresponding with **nickel tetrazincide,** $NiZn_4$, which was

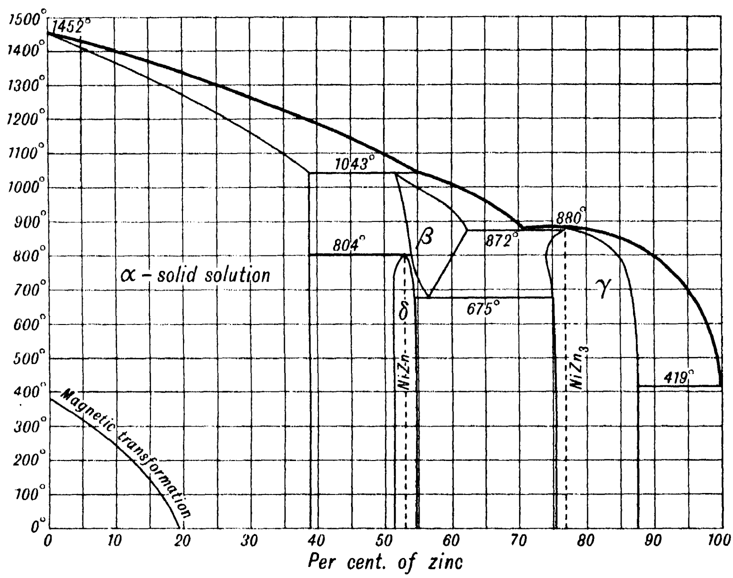


FIG. 129.—Freezing-point Curves of the Zinc-Nickel Alloys.

isolated in this way as a crystalline non-magnetic powder of sp. gr. 7·71, and melting approximately at 850°. This compound was rapidly attacked by 1 per cent. hydrochloric acid, leaving a magnetic deposit which was sometimes pyrophoric; the soln. generally contained zinc only. Dil. sulphuric acid attacked the alloy slowly, forming a soln. of the two sulphates, and depositing a magnetic powder. Nitric acid more conc. than 1 per cent. dissolved the alloy completely. Nickel chloride soln. dissolved the alloy on warming, giving rise to zinc hydroxide and a magnetic deposit. The e.m.f. of couples formed from mixtures of the two metals against zinc in various soln. showed breaks at 18·33 and 72·92 per cent. of nickel corresponding respectively with the tetrazincide and the tritazincide.

The **zinc-nickel-copper alloys** are found in commerce under various names: *nickelin, new silver, silveroid, silverite, Nevada silver, Potosi silver, Virginia silver, amberoid, electrum, arguzoid, white-copper,* etc. The term *maillechort*—after M. Maillet and M. Chorier, the first manufacturers of the nickel in France—is also used for a similar alloy. The alloy was for a long time known as *German silver, argent allemand,* or *argent d'allemagne;* but in 1914, the Alloys Nomenclature Committee suggested the alteration of the name since it is neither "German" nor "silver." The Committee proposed the term *nickel-silver.* The term German

silver has been in use so long, and is so familiar, that it is doubtful if the suggestion will displace the use of the term German silver. The alloy *pak-tong*—from the the Chinese *pai-t'ung*, meaning white copper—is a similar alloy. In the eighteenth century the term *pai-t'ung* was transcribed *petong*, and *pehtung;* and the word is also spelt *paaktong*, *packtong*, *pakfong*, and *packfong*. Paktong is the Cantonese dialect form of pai-t'ung. The word *packfong* is a scribal error introduced by G. von Engeström in 1776. One of the earliest references to the alloy occurs in A. Libavius, *De natura metallorum* (Francofurti, 1597), where he refers to a white bronze as *æs album*. There is an account of the alloy by J. du Halde in his *History of China* (London, 1736); by R. Watson in his *Chemical Essays* (London, 1781); and by J. B. Blake in the *Annual Register of the Society of Arts* (London, 1775). The history of the alloy was discussed by A. Bonnin, and F. R. Barton. The name *tombac*—a copper-zinc alloy—has the same origin, for it is a corruption of *tong-pack*. Packfong was used in early times in China for making gongs and other musical instruments, whence it was exported to Europe largely during the seventeenth and eighteenth centuries. G. von Engeström,[7] in 1776, and S. Rinman, in 1782, showed that paktong is a copper-zinc-nickel alloy. In 1822, A. Fyfe analyzed the Chinese alloy and gave a description of articles made from it. In 1823, Der Verein zur Beförderung des Gewerbfleisses—a Prussian Society for the Encouragement of Industry—offered a prize for the invention of an alloy which whilst similar to silver in appearance, should cost no more than one-sixth the price of silver, and be suitable for culinary and table-ware. In 1824, Henniger Bros., Berlin, prepared a copper-zinc-nickel alloy which they called *Neusilber*, and about the same time, A. Geitner, Schneeberg, prepared an analogous alloy which he called *argentan*. The alloys were manufactured in Vienna, by A. T. von Gersdorff, in 1825, under the trade-name *alpakka*.

Analyses of some of these alloys are indicated in Table VII. In the German silver

TABLE VII.—ANALYSES OF SOME COMMERCIAL NICKEL-COPPER-ZINC ALLOYS.

Cu	Ni	Zn		Cu	Ni	Zn	
67·00	19·30	13·60	O. Henry	54·00	18·00	28·00	P. A. Bolley
63·34	19·13	17·41	P. Louyet	53·30	26·60	20·10	A. Guettier
62·40	15·05	22·15	P. Louyet	51·60	26·00	22·40	A. Guettier
60·00	18·80	17·80	J. D. Smith (3·4 Co)	50·00	31·20	18·80	G. Frick
59·00	22·20	18·50	A. Guettier	50·00	18·75	31·25	J. P. J. d'Arcet
58·00	18·50	23·50	A. H. Hiorns	48·50	24·30	24·30	A. H. Hiorns
57·40	13·00	26·60	L. Elsner (3·0 Fe)	40·60	18·75	31·25	G. von Engeström
56·98	24·30	18·72	A. H. Hiorns	40·40	31·60	25·40	A. Fyfe (2·6 Fe)
55·20	21·40	23·40	A. Guettier	26·30	36·80	36·80	C. Keferstein

type of alloys the copper ranges from 50 to 66 per cent.; the nickel from 13 to 18 per cent.; and the zinc from 19 to 31 per cent. According to A. H. Hiorns, the percentage proportions respectively of nickel, copper, and zinc, used in Birmingham for German silver are: *extra white metal*, 30 : 50 : 20; *white metal*, 24 : 54 : 22; arguzoid, 20·5 : 48·5 : 31; *best best*, 21 : 50 : 29; *firsts* or *bests*, 16 : 56 : 28; *special first*, 17 : 56 : 27; *seconds*, 14 : 62 : 24; *thirds*, 12 : 56 : 32; *special thirds*, 11 : 56·5 : 32·5; *fourths*, 10 : 55 : 35; and *fifths* for plated goods 7 : 57 : 36. The silver-plated alloy was introduced as *alfenide*—after M. Alphen—and about 1840 it appeared as *china silver*, *christofle*, or *Christophle metal*. It has also been called *Peru silver*, *electroplate*, *arguroide*, etc. The silver plating of nickel was studied by G. Langbein, and A. McWilliam and W. R. Barclay. Some copper-nickel-zinc alloys are used as *solders* for nickel-silver alloys, and they often contain more zinc than the nickel-silvers—*e.g.*, the hard solders have 42 to 50; 38 to 47; 11 to 13·5; the medium solder, 56 : 34·5 : 9·5; and the soft solder, 56 : 36 : 8. S. Pearson and W. Prott patented the addition of 0·5 to 10·0 per cent. of nickel to brass;

and L. Guillet studied the properties of the *nickel-brasses*. The so-called *albata metal* is a nickel-brass. There are many other alloys containing small proportions of other metals. There is no hard-and-fast rule as to the names for particular alloys, and each manufacturer may employ, for trading purposes, specific terms of his own selection—*e.g.*, Table VIII. These alloys were discussed by W. T. Brannt, I. Cerkesoff, W. M. Corse, J. Cournot and E. Hiltbold, M. Duberget, W. C. Ellis and E. E. Schumacher, L. Elsner, A. M. Fairlie, A. T. von Gersdorff, H. W. Gillett, W. C. Gray and R. E. Ansell, A. H. Hiorns, M. Jähkel, H. Kloss, C. Künzel, J. Lardé, A. Ledebur, P. Louyet, R. Meslier, P. Reinglass, A. Rosenheim and E. Huldschinsky, C. Rothert and G. Dern, A. Rzehulka, M. Schied, O. Smalley, E. S. Sperry, A. C. Sturney, K. Styffe, E. R. Thews, and R. H. Thurston.

TABLE VIII.—SOME NICKEL-COPPER-ZINC ALLOYS.

	Cu	Ni	Zn	Other metals
Albata metal	40·0	8·0	32·0	
Alfenide	50 to 70	10 to 20	5 to 30	
Alpakka	65·2	13	19·5	
Aluminium-silver	57·0	20·0	20·0	and 3·0 Al.
Argozoil	54·0	14·0	28·0	and 2·0 each of Pb and Sn.
Argetan	50 to 70	10 to 20	5 to 30	
Arguzoide	48·5	20·5	31·0	
Aterite	55 to 60	12 to 18	13 to 20	Fe, 6 to 10; Pb, 1 to 2·5.
Carbonate silver	66	18	16	
China silver	65·24	13·0	19·5	As, 2.
Colorado silver	57	25	18	
Craig gold	80	10	10	
Electrum	51·5	26·0	22·5	
Keene's alloy	75	16	2·25	Fe, 1·5; Sn, 2·75; Al, 0·5; Co, 2.
Lutecin	80	16	5	Fe, 5; Sn, 2; Co, 1.
Maillechort	65·4	16·8	13·4	Fe, 3·4.
Malloydium	59·96	22·82	13·44	Fe, 0·95.
Markus's alloy	45·5	27·25	27·25	
Neogen	58	12	27	Sn, 2; Al, 0·5.
Nickel oroide	66 to 87	5 to 10	0 to 10	
Nickelin	55·3	31·1	13·1	Other varieties have 68 : 32 : 0; and 55·13 : 24·38 : 20·3.
Platinoid	54·04	24·77	20·42	Pb, 0·15; Fe, 0·47; Mn, 0·15.
Platinoid	60·0	14·0	24·0	1 to 2 Mn.
Parker's alloy	60	10	20	Cr, 10.
Rheotan	50·4	25·3	16·9	Fe, 4·5.
Silver bronze	58	16	23	Pb, 2; Sn, 1.
Silverine	71 to 79·5	16 to 16·5	1 to 7·5	Fe, 1 to 1·5; Sn, 1 to 2·75; Al, 0 to 0·5; Co, 1 to 2.
Sterline	68·52	17·88	12·84	Fe, 0·76.
Toucas's alloy	35·7	28·6	7·1	Fb, Fe, Sn, Sb—each 7·2.
Tumcaillant's metal	50·0	15·0	34·9	Al, 0·1.
Tutenay	45·7	17·3	37	
Victor metal	49·94	15·40	34·27	Fe, 0·28; Al, 0·11.
Wessell's silver	51 to 65	19 to 32	12 to 17	Ag, 2; Fe, 0·5.
White silver	55·2	20·7	24·1	

The most common impurities in nickel-silvers are derived from the metals employed, and, according to A. Fyfe, J. D. Smith, O. Henry, J. P. J. d'Arcet, P. Louyet, L. Elsner, F. C. Thompson, etc., they consist of small quantities of iron, lead, and tin. Small proportions of other elements may be deliberately added, and numerous mixtures have been patented. *E.g.*, those by Société Anonyme le Ferronickel, V. Schmidt, J. Coup and E. Allbaugh, C. F. Ackermann, etc. The general effect of a small proportion of *iron*—say 1 or 2 per cent.—is to increase the strength, hardness, and elasticity. Lead, and *tin* make the metal unsuited for rolling, but lead, to the extent of 2 or 3 per cent., is favourable when the

metal is cast and subsequently worked. *Carbon* improves the working qualities of the cold alloy, but when the temp. reaches 650° to 700° the carbon is liable to separate as graphite. F. C. Thompson found that oxygen may occur in the cast metal as a finely diffused oxide, probably zinc oxide. The addition of a deoxidizer, such as 0·5 to 1·5 per cent. of *manganese*, reduces the size of the crystal grains, and lessens the tendency to corrugation or " riffling " produced by adjacent crystals being thrust one over the other. M. le Thomas studied the *nickel-manganese brasses*. F. L. Sperry recommended 0·1 per cent. of *aluminium* as a deoxidizant; and J. W. Richards also recommended 2 to 3 per cent. of aluminium to produce a white, strong, elastic alloy. C. W. Leavitt found that with *magnesium* added as a metal wrapped in copper-foil, or as a magnesium-copper alloy, the mechanical properties, expressed in lbs. per sq. in., were greatly improved :

Cu : Ni : Zn	60 : 14 : 26		52 : 22 : 26		55 : 26 : 19		55 : 25 : 18	
Magnesium	None	0·1%	None	0·1%	None	0·1%	None	0·1%
Tensile strength	30,200	35,200	27,800	29,100	30,000	31,700	24,900	33,700
Elongation (per cent.)	2·5	8·5	3·5	10·75	7·0	11·0	7·25	12·25

A. Parkes, and A. M. Fairlie recommended small additions of *chromium ;* and the alloy *platinoid* may contain 1 or 2 per cent. of *tungsten.* W. Woolf and J. Andrews patented an alloy with antimony. According to E. A. Smith, the standard British coinage has Ag 50, Cu 40, Ni 5, Zn 5.

In some cases, the alloys are prepared by placing alternate layers of the three elements in a charcoal crucible, covering the mixture with charcoal, and melting the mixtures a rapidly as possible. One-third of the zinc and nickel is added in this way, and the remainder is introduced after the mixture has melted. The volatility of the zinc makes it difficult to get two batches to agree in composition. H. Kloss recommended a modification of this process. In another process, the separate metals are not employed, but they are used in the form of binary alloys. Part of the copper is alloyed with nickel (1 : 1 or 1 : 2) to form cupronickel, and part with zinc (1 : 2) to form brass. The brass is added to the cupronickel after it has been melted in a crucible—usually made of graphite. The nickel introduced as cupronickel dissolves in the molten brass more readily than does nickel alone. It is said that it is thus possible to produce a more homogeneous alloy, and to reduce the loss by the volatilization of zinc than when the separate metals are used. The molten mixture is stirred with a carbon or an iron rod. The iron-rod may be coated with a mixture of fireclay and borax. The preparation of the alloys was discussed by S. Kern, C. P. Karr, the Elektrostahl G.m.b.H., the Dürener Metallwerke, A. T. von Gersdorff, K. Styffe, and T. E. Kihlgren and co-workers. A. von Kügelgen discussed the preparation of the alloy by the use of roasted copper-nickel ore reduced by calcium chloride, and B. Neumann said that the equation: $3M_2O+CaC_2=3M_2+CaO+2CO$ more nearly represents the reaction than A. von Kügelgen's equation : $5M_2O+CaC_2=CaO+5M_2+2CO_2$, because the gaseous product contains approximately equal vols. of carbon monoxide and dioxide. B. Neumann considered that the carbon dioxide is due to a secondary reaction between the metal oxide and carbon monoxide.

G. Langbein obtained the alloy electrolytically from a soln. of copper and zinc sulphates in an aq. soln. of potassium cyanide, mixed with a soln. of nickel carbonate in aq. ammonia. C. L. Faust and G. H. Montillon studied the subject. M. Kugel used an electrolyte containing a strong mineral acid which is not changed by the current—*e.g.*, perchloric, perbromic or sulphuric acid—and also the salt of a light metal like magnesium, not changed by the current, in order to maintain the acidity of the baths without adding a fresh acid. Nitric acid, the halogen acids, and organic acids are not suitable. The anode consists of nickel-silver, and this maintains the composition of the bath constant as nickel-silver is deposited at the cathode.

According to H. le Chatelier, German silver behaves like a solid soln. which

suffers on heating a molecular transformation which shows a point of inflexion with a maximum and a minimum, on the electrical conductivity curve—*vide infra.* V. E. Tafel studied the ternary system, and he found that the ternary alloys liquate considerably so that the lower portions of the ingots become richer in nickel. The ternary diagram, Fig. 131, shows no signs of a ternary compound or a ternary eutectic. The surface of the temperature-concentration model consists of three surfaces each representing the separation of a series of primary solid soln. The third of these, the richest in zinc, is separated from the second by a eutectic line. The German silver type of alloys consist of homogeneous mixed crystals.

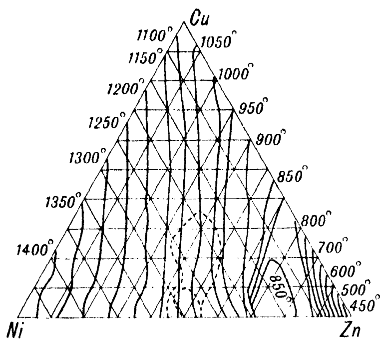


FIG. 130.—Isothermal Freezing-point Lines of the Nickel-Copper-Zinc Alloys.

V. E. Tafel found that the alloys containing 15·3 to 20·0 per cent. of nickel, 73 to 80 per cent. of copper, and 7 per cent. of zinc are remarkably like silver in colour when polished, and in ductility. The alloys with the zinc and copper, in the proportions approaching those of the brasses, are brass-yellow; those with a high proportion of zinc have the bluish-grey colour of zinc. H. Behrens observed the microstructure of the alloys. Alloys with 12 per cent. of nickel and 30 per cent. of zinc show greyish-white dendrites; the joints between the crystals are narrower, the higher the proportion of the Ni : Zn ratio the more marked is the network involving an intermediate substance, and, later

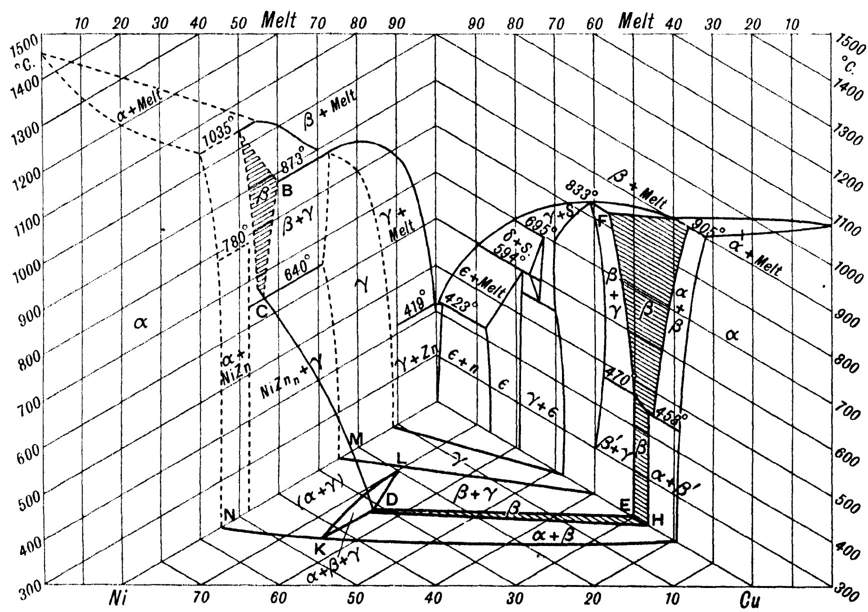


FIG. 131.—The Ternary System: Ni–Cu–Zn.

on, recrystallization sets in. The coring of the crystals in cast nickel-silvers is very persistent in the nickeliferous alloys, and this imparts brittleness to the metal. G. F. Geiger and R. E. Case discussed the colour of these alloys. The transformation of the structure to homogeneous or allotrimorphic crystals is produced by annealing—studied by O. F. Hudson, and F. C. Thompson. The

microstructure was examined by A. T. von Gersdorff, O. F. Hudson, F. C. Thompson, and V. E. Tafel. O. Bauer and M. Hansen investigated the ternary system, and Fig. 131 summarizes the results. It shows the relation of the ternary system to the three binary systems previously discussed. Observations were made by L. Guillet, J. Cournot, F. Adcock, O. Bauer and M. Hansen, K. Yamaguchi and K. Nakamura, V. E. Tafel, F. M. Ostroga, O. Smalley, and W. B. Price and C. G. Grant.

S. Kalischer said that nickel-silver shows no crystalline structure when made the electrode in a soln. of copper sulphate, but the crystalline structure is manifest when the metal is etched with nitric acid. E. F. Law showed that the microstructure closely resembles that of the brasses which consist of the α-solid soln. of the copper-zinc alloys. O. F. Hudson used a strongly acid soln. of ferric chloride as etching liquid. The microstructures of cold-rolled and annealed samples show that crystal growth occurs on annealing the alloys, but the cold-rolled alloy may show signs of the original cored structure of the cast material; and the cored structure is in evidence after 48 hrs.' annealing at 700°; but it had vanished after 72 hrs.' annealing at that temp. when the metal is virtually homogeneous. The extreme slowness of diffusion in German silvers as compared with the corresponding α-solid soln. of the copper-zinc alloys is attributed to the presence of nickel. The structure was studied by E. O. Jones and E. Whitehead, R. Genders, and O. Smalley.

I. Klemencic obtained alloys with a **specific gravity** ranging from 7·18 to 8·96; that of nickel-silver being 8·62; and that of nickelin, 8·96; and C. H. Lees, 8·665 for the alloy with Cu : Ni : Zn=62 : 15 : 22; and M. Weidig, 8·451 for the 59·89 : 20·15 : 19·9-alloy. F. C. Thompson found the sp. gr. of alloys at 17° to be:

Copper		60·6	61·8	61·6	55·7	61·2 per cent.
Nickel		7·6	16·4	22·4	17·4	28·6 ,,
Zinc		31·7	21·7	15·9	26·7	9·8 ,,
Hard worked	Sp. vol.	0·1169	0·1157	0·1140	0·1169	0·1145
	Sp. gr.	8·55	8·65	8·77	8·56	8·73
Annealed	Sp. vol.	0·1180	0·1162	0·1148	0·1173	0·1145
	Sp. gr.	8·48	8·60	8·71	8·52	8·74

The decrease in the **specific volume** with an increase in the nickel content is well-marked with both the annealed and work-hardened states. The values in the annealed state are consistently higher than in the work-hardened state. The addition of up to 1·5 per cent. of manganese has no practical influence on the sp. vol. although the deoxidized alloys have a higher sp. gr. The increase in sp. gr. due to an increase in the proportion of copper to zinc is clearly shown in alloys with about 15 per cent. of nickel. Argentan is said to be harder than silver, and V. E. Tafel added that alloys with 7 to 20 per cent. Cu, 33 to 40 per cent. Ni, and 40 to 52 per cent. of zinc are very hard. F. C. Thompson's values for Brinell's **hardness** were obtained with a load of 500 kgrms. and a ball 10 mm. in diameter. There is a very marked increase in the hardness at about 300° to 330°. The influence of nickel is to raise the temp. at which softening commences. This is shown by the following data:

Copper		60·6	61·8	61·6	55·7	61·2 per cent.
Nickel		7·6	16·4	22·4	17·4	28·6 ,,
Zinc		31·7	21·7	15·9	26·7	9·8 ,,
Hard rolled		130	130	134	167	158
Annealed	188°	158	155	155	185	167
	300°	185	185	176	203	195
	401°	130	158	150	167	174
	495°	92	130	143	109	143
	603°	80	88	93	88	130
	696°	64	70	73	70	95
	781°	62	64	74	66	88
	903°	48	61	72	58	80

Observations were made by C. A. Thompson. F. Robin studied the **acoustic properties** of a white alloy and observed that between 315° and 320° the curve of the duration of the sound which was progressively rising up to that temp. assumed an exceedingly rapid rise, and within an interval of 10 per cent. the duration of the sound increased to nearly fivefold. The variation in the resonance is so rapid that if the metal be struck continuously while cooling, the resonance may be heard to fall suddenly at a particular blow. The lowest curve relates to white metal fresh from the mill. The highest curve relates to the same bar reheated from about 500°. The middle curve is that of an annealed white metal (heated to 650° and cooled for 5 hrs. down to 150° or 200°). The bend in the curve due to the critical point is more accentuated in the curve of the annealed metal; stressing lessens it a good deal. Heating to 400° partly destroys the effect of stressing, but it is probable that the complete suppression of the critical point could not be noticed.

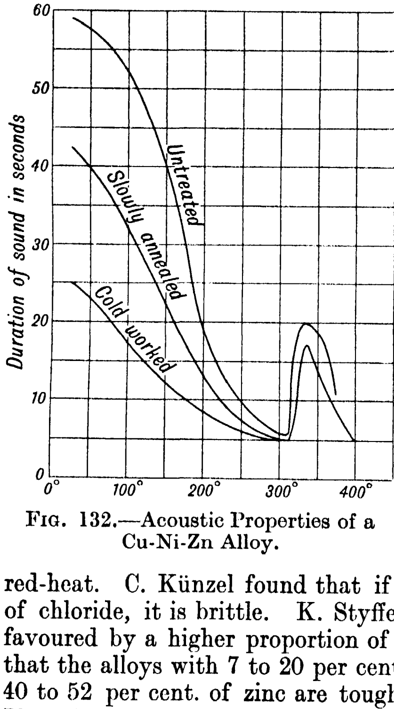


FIG. 132.—Acoustic Properties of a Cu-Ni-Zn Alloy.

V. E. Tafel found that alloys with 73 to 80 per cent. copper, 15 to 20 per cent. of nickel, and 7 per cent. of zinc are as malleable as silver; and K. Styffe added that the **malleability** is reduced by high proportions of zinc, and V. E. Tafel found that the **brittleness** attains two maxima—one with 27·3 per cent. of copper, 7·6 per cent. of nickel, 65·1 per cent. of zinc, and the other with 13·5 per cent. of copper, 16·4 per cent. of nickel, and 70·1 per cent. of zinc. A. Fyfe reported that the Chinese packfong becomes brittle when hammered at a dull red-heat. C. Künzel found that if the argentan contains 0·13 to 0·18 per cent. of chloride, it is brittle. K. Styffe found that the **toughness** of nickel-silver is favoured by a higher proportion of nickel—up to 20 per cent. V. E. Tafel found that the alloys with 7 to 20 per cent. of copper, 33 to 40 per cent. of nickel, and 40 to 52 per cent. of zinc are tough. According to S. Kern, the cast alloy with 70·0, 17·5, and 12·5 per cent. respectively of copper, nickel, and zinc had a **tensile strength** of 26 tons per sq. in., an elongation of 23 per cent. in 2 inches, and a bending test of 67° over a radius of 1⅝ inches; whilst with 70·0, 20·0, and 10·0 per cent. respectively of copper, nickel, and zinc, the tensile strength was 36 tons per sq. in. with an elongation of 14 to 17 per cent., and a bending test of 35° to 40° over a radius of 1⅝ inches. The fracture in both cases was fibrous. Observations were also made by C. Diegel, J. McNeil, J. Cournot and E. Hiltbold, G. F. Geiger and R. E. Case, and K. R. Koch and C. Dannecker. M. Weidig observed that the effect of annealing on a work-hardened alloy 59·89 per cent. copper, 20·15, nickel, and 19·9, zinc, and the tensile strength in kgrms. per sq. mm., the percentage elongation, and the **bending number**—*i.e.*, the number of completed bendings, through 90° and back over a radius of 5 mm., which can be completed without the appearance of a fracture, were:

	Hard alloy	400° air	400° water	600° air	600° water	800° air	800° water
Tensile strength	62·95	60·26	58·28	44·56	43·85	39·32	39·60
Elongation	4·9	10·8	10·8	34·25	31·85	36·5	36·0
Bending number	14·0	14·0	14·5	16·0	15·0	10·0	10·5

The most favourable annealing temp. is between 600° and 700°. F. C. Thompson

obtained the following results for the tensile strengths and compressive strengths of cast bars expressed in tons per sq. in.:

	Copper	60·6	61·8	61·6	55·7	61·2 per cent.
	Nickel	7·6	16·4	22·4	17·4	28 6 ,,
	Zinc	31·7	21·7	15·9	26·7	9·8 ,,
Tensile	Yield-point	7·16	9·00	8·52	9·04	8·76
	Max. stress	16·88	17·80	17·20	17·12	19·72
	Elongation	34·5	39·5	24·5	33·5	32·0 per cent.
	Reduction	37·2	32·7	26·7	37·8	36·7 ,,
Compressive	Elastic limit	6·0	7·0	10·0	7·25	8·0
	Elastic modulus	6450	9800	4300	5630	8030
	Stress to compress to ½ height	74·8	78·5	74·0	81·2	84·0
	Compression	57·2	56·2	57·8	55·2	55·0 per cent. at 100 tons per sq. in.

F. C. Thompson observed that a remarkably small change is produced in the mechanical tests by alterations of composition. The alloys are gradually hardened by increasing proportions of nickel, but not so much as might have been expected. The hardening shown in the results for the yield-point, and maximum stress in tension, and the true **elastic limit** in compression find no counterpart in the ductility columns since this undergoes very little change. The introduction of up to 1·5 per cent. of manganese has a beneficial influence, for it increases the ductility without a loss of strength. The values for the **elastic modulus** for compressive stresses are irregular. This is attributed to the differences of casting temp., rate of cooling, and cooling stresses in the cast alloys. A. Gray and co-workers gave $1·3046\times10^{12}$ dynes per sq. cm. for **Young's modulus** at 20·3°, and $1·2701\times10^{12}$ at 86·9°. The diminution per degree is therefore 0·000397. For the elastic modulus of cast nickel-silver, A. Gray and co-workers gave 13,300 kgrms. per sq. mm.; and W. Pscheidl, 12,094; and for the drawn metal, S. Katzenelsohn gave 11,449 kgrms. per sq. mm.; and G. Searle, 11,550. For Poisson's ratio, J. R. Benton gave 0·371, and for nickelin, 0·403. W. G. Brombacher and E. R. Melton, H. J. French and W. A. Tucker, L. Guillet, G. H. Keulegan and M. R. Houseman, K. R. Koch and C. Dannecker, F. M. Ostroga, W. B. Price and P. Davidson, C. Rothert and G. Dern, O. Smalley, E. R. Thews, G. L. Thirkell, F. C. Thompson and E. Whitehead, and L. J. Wood and S. W. Parr studied the mechanical properties of these alloys.

F. C. Thompson observed for the **torsion strength** represented by the number of complete rotations or twists which a wire can endure:

	Copper	60·6	61·8	61·6	55·7	61·2 per cent.
	Nickel	7·6	16·4	22·4	17·4	28·6 ,,
	Zinc	31·7	21·7	15·9	26·7	9·8 ,,
Hard drawn		2·5	2·5	1	2	14
Annealed	100°	6·5	21	3	1·5	9·5
	293°	2·0	2	5·5	1·5	14·5
	405°	42	29	7·5	2·5	23
	499°	48	50	15	39	32
	589°	53	62	101	50	49
	696°	81	76	115	71	98
	797°	84	86	119	70	79

The number of twists which are possible with the hard-drawn wire is very small, and little improvement occurs until recrystallization commences. The ductility then rapidly increases, and with it, the resistance to torsion. A flattened maximum appears on the curve, after which, the alloy begins to burn, and the number of twists falls off again. There is a gradual rise in the temp. at which annealing commences as the proportion of nickel is increased. The results with fully annealed alloys containing up to 1·5 per cent. of manganese show that deoxidation with manganese improves the alloys. A. Gray and co-workers gave $3·4256\times10^{11}$ dynes per sq. cm. for the **modulus of rigidity** of nickel-silver at 20·7°, and

$3{\cdot}3033 \times 10^{11}$ at 88·3°, so that the diminution is 0·000528 per degree. The effect of temp. on the rate of subsidence of torsional vibrations, Fig. 133, shows that the rate of dying out of the amplitude is faster at the lower temp. This is the reverse of that found with wires of other metals. G. Subrahmanyam calculated the logarithmic decrement; and G. H. Keulegan and M. R. Houseman measured the temp. coeff. of the rigidity; S. Sato, the latent energy due to cold work.

F. C. Thompson found that **alternating stress** tests with some commercial alloys furnished the following results:

Copper		60·08	61·25	55·60	58·38	55·49 per cent.
Nickel		9·91	10·25	12·17	18·77	23·06 ,,
Zinc		28·31	27·42	31·43	22·37	20·66 ,,
Hard rolled		534	110	115	51	44
Annealed	300°	460	70	67	35	41
	370°	386	82	70	35	42
	440°	328	79	130	45	42
	510°	803	255	280	107	28
	650°	1100	315	416	268	158
	785°	1387	326	382	257	200
	860°	1414	312	357	306	176
	930°	1023	170	255	262	73
Cooled slowly from	950°	1431	362	360	260	—

All the samples become less ductile between 300° and 400°. The increased hardness produced by an increased proportion of nickel is shown by the smaller number of alternations endured by the alloys with a high proportion of nickel. The alloys deteriorate when they are heated to a high temp. and cooled in air. The cooling

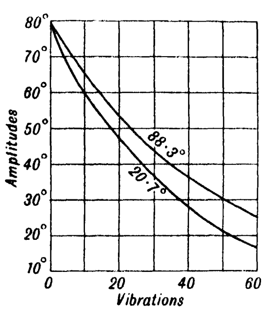


FIG. 133.—The Effect of Temperature on the Damping of Torsional Oscillations.

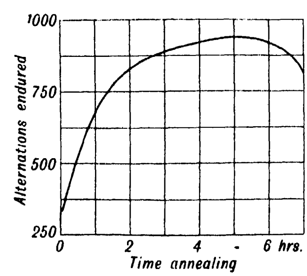


FIG. 134.—The Effect of the Duration of Annealing on the Resistance to Alternating Stresses.

of the alloys in a muffle from 930° improves their resistance to alternating stresses. Impurities usually present in commercial alloys have very little influence on their hardness, and resistance to alternating stresses. The tendency of the alloys to burn is increased by increasing the proportion of nickel, by increasing the ratio Zn : Cu, and by increasing proportions of impurities present in the alloys. The general effect of the duration of annealing on this resistance of these alloys to alternating stresses is illustrated by the curve in Fig. 134. This steadily rises from about 693 after 1 hr.'s annealing to about 933 after 4 hrs.' annealing. The same result is obtained with 6 hrs.' heating, but after 7 hrs.' annealing the metal becomes more brittle and less ductile. The influence of the rate of cooling is illustrated by an alloy with 10 per cent. of nickel, and 61 per cent. of copper. The samples cooled very slowly or very quickly are the most ductile and the softest, whilst the others are harder and not so tough:

	Alternations endured	Brinell's hardness
Cooled slowly in closed pot from 800°	932	47
Cooled in thin strips in air from 720°	343	63
Quenched in water from 370°	427	55
Quenched in water from 720°	444	53

D. J. McAdam gave the following fatigue test of an annealed copper-nickel-zinc alloy with Cu : Ni : Zn=74·01 : 19·45 : 5·17, expressed in lbs. per sq. in.: Tensile strength, 51, 100; torsional strength, 43, 900; shearing strength, 35, 600; endurance limit (rotating) 20, 800; and endurance limit (alternating torsion), 13,000.

F. Pfaff found that the coeff. of **thermal expansion** of nickel-silver is $0·0_41836$ between 0° and 100°; and A. Gray and co-workers, $0·0_5654$. G. R. Dahlander observed that the coeff. of thermal expansion between 0° and 100° increases from $0·0_417011$ with a load of 1·250 kgrms. in tension, to $0·0_417913$ with a load of 7·5 kgrms. J. Disch gave for the linear expansion of electrum, at $\theta°$ between 0° and 300°, in mm. per metre, $\delta l = 2·824\theta + 0·0165\theta^2$, or, zero at 0°, 2·84 at 100°, 5·71 at 200°, and 8·62 at 300° According to F. Wüst, the cooling curve of the following alloys shows two breaks, and the freezing is attended by an expansion attaining 0·045 per cent. as a maximum; whilst a contraction begins between 920° and 1000°, thus,

Cu : Ni : Zn	Break in cooling curve: First	Break in cooling curve: Second	Expansion: Begins	Expansion: Maximum (per cent.)	Contraction: Begins	Contraction: Maximum (per cent.)
61·57 : 16·10 : 22·16	1020°	955°	1068°	0·045	917°	2·025
56·20 : 20·40 : 23·36	1060°	1025°	1049°	0·39	924°	2·050
51·40 : 26·22 : 22·30	1087°	800°	1080°	0·027	949°	2·030
46·10 : 35·80 : 18·00	1085°	—	1090°	0·032	1010°	1·935

According to L. Lorenz, the **thermal conductivity** of nickel-silver is 0·0700 c.g.s. units at 0°, and 0·0887 at 100°; G. Wiedemann and R. Franz gave 0·063 at 12·5°; C. H. Lees gave for the Cu : Ni : Zn=62 : 15 : 22 alloy, 0·0415 at −160°, 0·049 at −80°, 0·056 at 0°, and 0·0595 at 18°; and A. C. Mitchell, 0·0068 at 0°, 0·0082 at 100°, 0·0096 at 200°, and 0·0110 at 300°. L. C. Bailey gave for the thermal conductivity:

	−170°	−150°	−50°	0°	50°	150°	250°	450°
k	0·039	0·041	0·051	0·058	0·066	0·085	0·102	0·118

Observations were made by T. Barratt and R. M. Winter. G. Glage gave 0·131 at 80° for the temp. conductivity, and 0·106 for the inner heat conductivity of nickel-silver. H. Tomlinson gave 0·09464 for the **specific heat** of nickel-silver between 0° and 100°; and A. Campbell observed that the sp. ht. increases 0·009 per cent. per degree between 16° and 80°; 0·0115 per cent. at 127°; 0·0182 per cent. at 142°; 0·0297 per cent. at 181°; and 0·0505 per cent. at 262°. Observations were made by H. Esser and co-workers. M. Weidig found the **melting point** of the Cu : Ni : Zn=59·89 : 20·15 : 19·9-alloy to be 1123°. G. Frick observed that nickel-silver melts at a bright red-heat, and in air, the zinc is oxidized; whilst H. Behrens noted that nickel-silver melts more easily than cupronickel, and no spitting occurs in the casting of the molten metal. According to A. R. Haslam, if wires of the alloy be heated to redness in hydrogen, the less the proportion of nickel in the alloy, the greater is the loss of zinc. Thus, in 6 hrs., 2·258 grms. of an alloy with 11·4 per cent. of nickel lost 0·274 grm., and with 17·6 per cent. of nickel, 0·182 grm. W. H. Preece, and F. H. Cinget observed the strength of electric current required to melt wires of nickel-silver. The **freezing point** curves of the alloys are illustrated in Fig. 130. They are obtained from V. E. Tafel's data:

Copper	81·7	81·2	73·6	73·5	73·5	63·0	61·9 per cent.
Nickel	11·8	13·2	19·4	13·8	7·5	26·6	14·3 ,,
Zinc	6·5	5·6	7·0	12·7	19·0	10·4	23·8 ,,
Freezing begins	1095°	1133°	1168°	1104°	1036°	1195°	988°
Freezing ends	1045°	1072°	1113°	1031°	969°	1104°	928°

Copper	60·2	60·4	53·7	51·1	47·2	44·0	39·9 per cent.
Nickel	33·9	6·7	39·4	7·8	45·4	17·3	27·1 ,,
Zinc	5·8	32·2	6·9	41·1	7·4	38·7	33·0 ,,
Freezing begins	1224°	962°	1253°	922°	1277°	947°	915°
Freezing ends	1125°	893°	1166°	—	1189°	—	—
Break in cooling	—	—	—	907°	—	911°	910°

Copper	38·9	40·5	33·9	33·8	30·2	33·6	33·4 per cent.
Nickel	23·6	8·0	60·9	33·6	34·5	19·4	7·3 ,,
Zinc	37·5	51·5	5·2	32·6	35·3	47·0	59·3 ,,
Freezing begins	999°	872°	1326°	1110°	1037°	951°	846°
Freezing ends	—	851°	1230°	1011°	908°	—	830°
Break in cooling	913°	573°	—	—	651°	924°	632°

Copper	26·7	27·1	27·6	22·6	26·8	27·3	19·6 per cent.
Nickel	67·0	40·9	33·0	36·7	14·4	7·6	75·8 ,,
Zinc	6·3	32·0	39·4	40·7	58·8	65·1	4·6 ,,
Freezing begins	1347°	1134°	1076°	989°	860°	843°	1361°
Freezing ends	1252°	1015°	961°	928°	827°	807°	1267°
Break in cooling	—	633°	698°	725°	790°	—	—

Copper	20·8	20·2	20·0	19·5	13·5	13·2	9·7 per cent.
Nickel	39·3	26·5	22·6	9·1	81·6	34·2	36·1 ,,
Zinc	39·9	53·3	57·4	71·4	4·9	52·6	54·2 ,,
Freezing begins	1099°	946°	887°	829°	1373°	984°	853°
Freezing ends	969°	882°	847°	762°	1302°	875°	—
Break in cooling	727°	390°	773°	—	—	964°	843°

Copper	14·5	6·1	5·0	6·9	6·9	6·9 per cent.
Nickel	14·4	89·1	71·1	49·5	26·8	6·7 ,,
Zinc	71·1	4·8	23·9	43·6	66·3	86·4 ,,
Freezing begins	859°	1394°	1297°	1102°	886°	773°
Freezing ends	822°	1336°	1199°	—	—	—
Break in cooling	—	—	—	851°	839°	496°

H. Esser and co-workers gave 67·8 to 69·1 cals. per gram for the latent heat of fusion. E. Salles found that the nature of the metal walls—nickel-silver, brass, or steel—had no effect on the coeff. of diffusion of gaseous ions. R. Emden observed that the emission of light from nickel-silver begins at 403°.

According to K. Feussner and St. Lindeck, the **electrical resistance** of the nickel-silvers is much greater than that of copper; it varies with the temp. of annealing; and after a prolonged heating at 150°, the resistance becomes smaller. W. H. Stannard gave a table of the resistance of nickel-silver. F. Kohlrausch pointed out that the resistance is great enough for the metal to be employed in making normal resistance coils. The observations of G. Frick and M. Müller, H. Buff, A. Matthiessen, P. T. Riess, and G. Wiedemann show that the resistance of nickel-silver is about 13 or 14 times greater than that of silver; and A. Arndtsen gave 18·72 for the conductivity of the Cu : Ni : Zn=61·65 : 15·75 : 22·60-alloy when that of silver is 100. A. Emo added that the electrical conductivity of nickel-silver at 0° is 6·438 per cent. of that of silver; A. Oberbeck and J. Bergmann found that it is 6·95 times as small as that of mercury; and W. M. Mordey, that it is 8·88 times as small as that of copper. A. A. Sommerville's results for the effect of temp. on the resistance of nickel-silver are summarized in Fig. 135. A. Emo said that the absolute resistance of nickel-silver is $0·0_4 22922$; F. Uppenborn added that the resistance of nickelin at 0° is 0·4117 ohm—temp. coeff. 0·00028; and of nickel-silver, 0·2670 ohm—temp. coeff. 0·00034 to 0·00047. K. Feussner and St. Lindeck found that the resistance of nickelin with Cu : Ni : Zn=61·63 : 18·46 : 19·67 is 33·2 micro-ohms—temp. coeff. 0·0030, and of nickel-silver with 60·16 : 14·03 : 25·37, 30 micro-ohms—temp. coeff. 0·00036. I. Klemencic said that the resistance of nickel-silver is 3·84 times as great as that of mercury, and nickelin, 2·90 times as great—the temp. coeff. are respectively 0·000380 and 0·000185 per degree between 0° and 16·5°. Observations were also made by E. L. Lederer, G. Wuckel, and A. Schulze. W. Meissner studied the super-conductivity at low temp.; and L. Guillet and M. Ballay, the effect of cold-work.

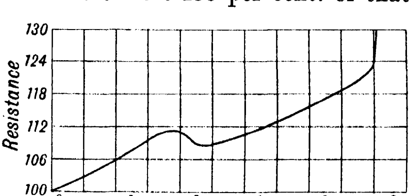


FIG. 135.—The Effect of Temperature on the Resistance of Nickel-Silver.

H. le Chatelier observed a peculiar change in the electrical resistance of nickel-silver at 300°, due, he thought, to a molecular transformation. He thought that the change occurs with extreme slowness over a range of 150°. F. Robin did not confirm this, for he was able to detect the change with fairly rapid heating, and it occurred with remarkable abruptness, Fig. 135. This change is connected with the instability of electrical resistances constructed of these wires. The heat generated by the current may raise the temp. of the wires to the transformation point, and mechanical brittleness may be thus induced which makes fracture easy. The same change may be responsible for annealing cracks. F. C. Thompson argued that if the transformation be due to nickel, its intensity should be approximately proportional to the nickel content of the alloy, but this is not the case. It was therefore inferred that the phenomenon is due to the relationship between nickel and zinc, that is, to the polymorphic transformation of a nickel zincide—probably $NiZn_3$. The bulges in the curves are in agreement with A. Smit's assumption that in work-hardened metals an irreversible change of molecular constitution is induced by press., and nickel trizincide when subject to a severe stress may undergo a corresponding transformation which is not reversed when the stress is removed, but is lost on re-heating to 300° or 400°. According to O. D. Chwolson, the resistance of hard-drawn nickel-silver decreases by about 1·1 per cent. with a gentle annealing, and increases by about 2 per cent. on strongly annealing the alloy. J. Bergmann observed that an hour's heating of the alloy at 300° makes the resistance about 0·13 per cent. smaller than before. F. C. Thompson measured the resistance, *R* ohms, of alloys at about 16°. The wires were 3 to 4 inches long and 0·001 inch in diameter ; the wires were hard drawn, and then annealed at the temp. indicated :

Copper		60·6	61·8	61·6	55·7	61·2 per cent.
Nickel		7·62	16·4	22·4	17·4	28·6 ,,
Zinc		31·7	21·7	15·85	26·7	9·81 ,,
R	Hard drawn	22·2	30·2	32·6	27·5	41·5
	Annealed 100°	21·6	30·5	32·8	27·7	41·6
	293°	21·1	30·4	32·5	28·0	42·0
	332°	20·7	31·5	33·8	28·6	42·2
	353°	19·3	31·5	34·2	28·4	41·7
	381°	18·8	31·8	34·5	28·0	41·5
	405°	18·3	30·6	32·6	27·5	40·9
	430°	18·2	30·0	32·5	27·4	41·0
	453°	17·9	30·5	33·5	26·8	40·9
	538°	18·6	30·5	33·5	27·3	40·9
	646°	19·5	30·3	33·1	27·1	41·1
	797°	19·2	29·8	34·0	27·6	41·3

The results are plotted in Fig. 136, and they show that the electrical resistance increases as the proportion of nickel increases. Indeed, nickel so dominates the results that in the fully annealed state, the sp. resistance of the alloys is independent of the Cu : Zn-ratio, and is well-expressed by the linear relation, $R=12+\text{Ni}$ micro-ohms per c.c., where Ni represents the percentage amount of nickel present. The presence of up to 1·5 per cent. of manganese apparently lowers the sp. resistance, and this may be regarded as a result of deoxidation. The resistances of the hard-drawn and fully annealed alloys closely correspond with one another. Only the alloys with 7·5 per cent. of nickel show the usual decrease in resistance produced by recrystallizing a hard-worked metal. M. Weidig observed that for the 59·89 : 20·15 : 19·9-alloy, the electrical resistance, *R* ohms for a wire 3 mm. diameter, and 1 metre long, and

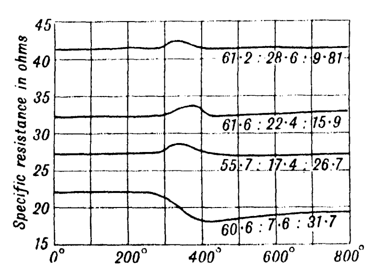


FIG. 136.—The Effect of Annealing on the Electrical Resistance of Cu : Ni : Zn-Alloys.

hard-drawn, is 0·04763 ; when completely softened, 0·04465 ; and when annealed at different temp.,

	400°		600°		800°	
Cooled in .	air	water	air	water	air	water
R . .	0·04444	0·04392	0·04386	0·04411	0·04565	0·04387

J. Dewar and J. A. Fleming found that the curve representing the variation of the resistance from −182° to 99·3° is linear ; and G. Niccolai found for the resistance, R c.g.s. units, of nickel-silver, and nickelin :

	400°	300°	200°	100°	0°	−100°	−189°
Nickel-silver .	31,610	31,184	30,341	29,393	28,457	27,538	26,718
Nickelin . .	38,640	38,470	37,787	37,000	36,200	35,402	34,692

R. Benoit represented the resistance at the temp. $\theta°$ by $R=R_0(1+0{\cdot}00035660\theta)$; and A. Matthiessen and C. Vogt gave for the electrical conductivity $7{\cdot}803-0{\cdot}0034619\theta+0{\cdot}0_6395\theta^2$ for the 30·593 : 12·84 : 6·56-alloy, when the conductivity of hard-drawn silver is 100. J. Götz observed that with hardened wires, and increasing current strengths, the resistance first rises, and then falls to its initial value. R. S. Willows found that the resistance of nickel-silver is the same for alternating as it is for direct currents at 20°, 100°, the temp. of liquid carbon dioxide and of liquid air. W. H. Preece, and F. H. Cinget studied the heating effects, and the safe carrying capacities of wires for the electric current ; and A. Campbell, the Joule heating effect of the current. The relations between the electrical and thermal conductivities were studied by F. E. Neumann, P. G. Tait, and L. Lorenz ; and the effect of a load on the resistance, by H. Tomlinson, and J. G. MacGregor.

C. Dannecker found the **thermoelectric force,** E millivolts, of a couple of nickel and nickel-silver with the cold-junction at 0°, to be :

	−185°	−80°	0°	100°	200°	400°	600°	800°	900°
E .	−0·8	−0·4	0	−0·6	−1·1	−0·4	−2·5	−5·1	−6·5

J. Dewar and J. A. Fleming gave for the e.m.f., E c.g.s. units, of a couple of lead and nickel-silver with the cold-junction at 0°,

	100°	26·2°	12·5°	−12·4	−61·0°	−162·4°	−203·1°
E .	−125,050	−28,820	−13,570	+13,070	+58,180	+124,670	+141,905

E. Noll obtained with this couple −14·68 microvolts at 50°. For the couple of copper and nickel-silver, K. Feussner and St. Lindeck observed 14·4 microvolts per degree difference of temp. ; and with copper and nickelin, I. Klemencic obtained 11·47 microvolts between 0° and 100°. The subject was discussed by F. Peters, and L. J. Neuman. F. C. Thompson found for the hard-soft couple—*i.e.*, one made from hard-drawn and annealed wires—the results plotted in Fig. 137. The neutral point at 150° for the 60·6 : 7·6 : 31·7-alloy is on a curve which rises to 380°, when a sharp break occurs. The other curves show discontinuities at 410°, and 420°, corresponding with the temp. at which the softening of the alloy begins. M. Maclean measured the effect of a longitudinal tensile stress on the thermoelectric force, and found for nickel-silver wires—one of which had been permanently elongated by longitudinal stress—0·1027 microvolt per degree difference of temp. in hot and

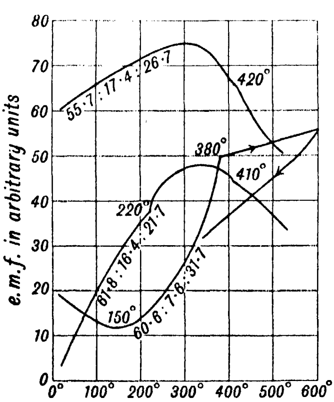


FIG. 137.—Thermoelectric Force of Hard-Soft Couples of Cu-Ni-Zn-Alloys.

cold junction; and for a couple with one wire loaded—the current passes from the stretched to the unstretched wire:

Total load	250	500	750	1000	1250	1500	1750 grms.
Temporary elongation	—	0·08	0·105	0·13	0·18	0·35	0·80 per cent.
Permanent elongation	—	—	—	—	0·051	0·162	0·588 ,,
Microvolt per degree	0·0679	0·0634	0·0661	0·0813	0·0996	0·1059	0·122

G. Borelius observed that the **Peltier effect** with copper and nickelin at 0° is 1·236 millicals. per coulomb, and with copper and nickel-silver, 1·650 millicals. per coulomb. A. Campbell observed that the neutral point with a couple of nickel and nickel-silver is about 252·3° to 254·3°; and he studied the effect with iron and nickel-silver. G. Borelius also obtained for the **Thomson effect** with nickelin, at 31°, −17·14 microvolts per degree, and with nickel-silver, at 23°, −10·45 microvolts per degree. A. Battelli found that the Thomson effect is proportional to the current strength and the temp. on the absolute scale. H. E. Smith studied the effect of strain on the Thomson effect of German silver.

G. Frick said that nickel-silver is not **magnetic,** or only slightly so, when it is contaminated with iron. A. Kussmann and H. J. Seemann studied the paramagnetism of these alloys. V. E. Tafel found that what he called the A-crystals become magnetic when the alloy solidifies. E. d'Agostino observed magnetostriction with transverse magnetization.

G. Frick observed that when nickel-silver is exposed to air it acquires a yellow tarnish; and A. Ledebur, that the molten metal absorbs oxygen. A. Wagner found that nickel-silver with 70·2 per cent. of copper, in the absence of carbon dioxide, is less energetically attacked by soln. than is the case with brass or bronze; aq. soln. of ammonium alkali, and magnesium chlorides have the most vigorous attack in the presence of carbon dioxide; but A. Vogel observed no action on the alloy immersed in potash-lye (1 : 500). G. E. Buttenshaw obtained an alloy with 41 to 43·86 per cent. of copper, 10 to 10·20 per cent. of nickel, and 40 to 43·19 per cent. of zinc with small proportions of lead, tin, aluminium, and phosphorus, which, when in contact with iron, is not attacked by sea-water. J. Jahn found that in contact with hydrogen sulphide at

	100°	150°	199°	262°	292°	
Tombac	861·8	866·8	867·9	866·3	882·1	mgrms.
Gain in weight	0·2	1·2	1·4	3·9	7·4	,,
Nickel-silver	834·3	835·9	834·3	836·6	833·2	,,
Gain in weight	0	0·6	0·9	3·6	5·9	,,
Nickelin	846·7	826·0	818·3	826·2	844·7	,,
Gain in weight	0·4	0·4	0·3	3·6	13·5	,,

Tombac is a zinc-copper (80·3 to 97·8 : 2·2 to 15) alloy with or without lead. Again, with moist and dry sulphur dioxide, at

		100°	159°	202°	245°	297°	
Moist	Tombac	841·9	850·3	845·2	847·5	836·2	mgrms.
	Gain in weight	0·4	0·2	0·2	0·1	0·3	,,
Dry	Tombac	850·8	848·3	847·8	838·2	855·3	,,
	Gain in weight	0·3	0·5	0·4	0·4	0·4	,,
Moist	Nickel-silver	834·5	832·9	833·5	832·9	832·7	,,
	Gain in weight	0	0	0	0·1	0·1	,,
Dry	Nickel-silver	830·1	830·5	832·3	831·5	832·0	,,
	Gain in weight	0·2	0·2	0·3	0·1	0·1	,,
Moist	Nickelin	842·6	844·1	845·7	843·7	843·6	,,
	Gain in weight	0·1	0	0·1	0·1	0·2	,,
Dry	Nickelin	844·1	837·3	843·6	843·9	841·3	,,
	Gain in weight	0·1	0·5	0·2	0	0	,,

E. Harbeck observed that nickel-silver anodes are not attacked by sulphuric acid of sp. gr. 1·53; A. T. von Gersdorf found that nickel-silver becomes white when it is boiled with sulphuric acid (1 : 7); whilst E. S. Sperry found that dil. nitric acid dissolves superficially the copper and zinc and makes the nickel passive. G. Frick found that when nickel-silver is immersed in vinegar, it becomes coated

with verdigris only in those parts where air has access; and J. P. J. d'Arcet, that it becomes greenish-black in vinegar; in wine, it becomes dark brown; in a soln. of sodium chloride, reddish-brown; in a soln. of tartaric acid or ammonium chloride, black with green spots; and in oxalic acid, black. M. V. Ruisakoff and I. N. Buschmakin studied the action of phosphorus and of phosphoric acid. A. Gawalowsky observed that crude petroleum, and mineral oils have no action on nickel-silver, but rape oil, and 4 per cent. vinegar attack it strongly. J. I. Crabtree and G. E. Matthews observed that hydroquinone or pyrogallol developing baths, and sodium thiosulphate or hypo-fixing baths, corrode nickel-silver, and aterite alloys. W. H. Finkedey, R. J. Anderson and G. M. Enos, F. Sprinkmeyer, F. Orme, L. J. Wood and S. W. Parr, and W. Voigt studied the corrodibility of the alloys. H. A. Trebler and co-workers studied the action of milk on the alloys. G. J. Fowler and P. J. Hartog studied the **silver-nickel-zinc alloys.**

T. Fleitmann [8] observed that 10 per cent. of cadmium can be added to nickel without it losing its working qualities. G. Voss prepared **nickel-cadmium alloys** and found that the volatility of the cadmium prevented the diagram beyond 15 per cent. of nickel from being explored. Nickel does not form solid soln. with cadmium at the m.p. 321°. At 501°, a compound of unknown composition reacts with the mother-liquor to form **nickel tetracadmide,** $NiCd_4$. C. E. Swartz and A. J. Phillips detected a hard constituent, **nickel heptacadmide,** $NiCd_7$, in the alloys. These alloys are non-magnetic. A. Westgren and W. Ekman showed that **nickel pentitahenicosicadmide,** Ni_5Cd_4, can be prepared as with the analogous compounds of iron, and cobalt zincides. A. J. Bradley discussed the X-radiograms. A. Roux and J. Cournot found that the electrodeposited alloy contains solid soln., not mixtures. J. Cournot studied the non-magnetic alloys of the two elements.

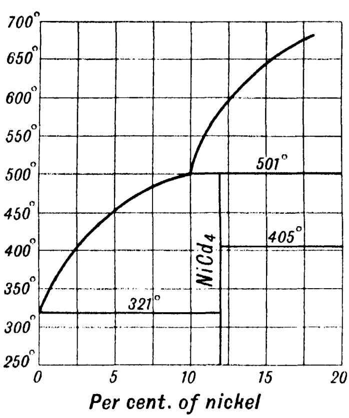


FIG. 138.—Freezing-point Curves of Nickel-Cadmium Alloys.

M. Ekker and J. Krajesics prepared a **nickel-copper-cadmium alloy,** or rather an alloy with part of the zinc in nickel-silver replaced by cadmium—Cu, 1000; Ni, 600; Zn, 400; Cd, 30; Mg, 10; Sn, 2; and Al, 1—which was thought to maintain its lustre in air at 100°, and to be acid proof.

J. Nicklès [9] observed that nickel does not unite directly with mercury. R. Böttger prepared **nickel-mercury alloys,** or **nickel amalgams** from sodium amalgam and a soln. of nickel chloride. The reaction is attended by the development of heat, the liberation of hydrogen, and the precipitation of nickelous hydroxide. H. Moissan employed a similar process. J. Bellucci and R. Corelli reduced a soln. of potassium nickelous cyanide by sodium amalgam in an atm. of hydrogen; A. Damour reduced a soln. of nickelous amminochloride with zinc amalgam; and J. Schumann, a soln. of nickelous chloride with zinc amalgam. If a soln. of nickelous nitrate be similarly treated, only nickelous hydroxide is formed. P. Casamajor obtained nickel amalgam by shaking up nickel with sodium amalgam and dil. acid. J. Schumann, and W. Ramsay obtained the amalgam by the electrolysis of a soln. of nickel chloride with a mercury cathode. G. Tammann and co-workers found the solubility of nickel in mercury to be $5{\cdot}9\times10^{-4}$, and N. M. Irvin and A. S. Russell, $<2\times10^{-5}$ grm. per 100 grms. of mercury.

R. Böttger said that the viscid amalgam is non-magnetic; A. Damour, and C. P. Steinmetz found that the nickel amalgams are magnetic. J. Schumann also found that the amalgam is non-magnetic. A. Damour noted that when heated, the mercury is distilled off, leaving ash-grey, spongy nickel, which, according to H. Moissan, is not pyrophoric. A. Damour observed that when nickel amalgam

is exposed to air, the nickel is oxidized to black nickelous oxide ; and H. Moissan also noticed that the amalgam is readily oxidized in air or in water. A. S. Russell and co-workers studied the order of the removal of metals from amalgams by oxidizing agents, and found Zn, Cu, Cr, Fe, Mo, Co, Hg, Ni, W. M. Rabinovich and P. B. Zywotinsky found that nickel is dispersed in mercury above the solubility limit to form a colloidal soln. E. Palmaer gave 0·00014 per cent. for the solubility of nickel in mercury, and the subject was discussed by R. Brill and W. Haag. G. Tammann and W. Oelsen found for an amalgam with 0·144 per cent. of nickel, the sp. magnetization 0·198 gauss. Observations were also made by D. Wünsche. C. F. Schönbein observed that when the amalgam is shaken in air, or in water acidified with sulphuric acid, some hydrogen dioxide is formed. R. Böttger observed that no gas is developed when the amalgam is placed under water or dil. acid ; and, added A. Damour, the amalgam dissolves very slowly in cold, dil. sulphuric or hydrochloric acid, and in hot acid, the nickel is dissolved. The amalgam is completely soluble in nitric acid.

H. Giebelhausen [10] found that amorphous boron dissolves in nickel ; I. Fetchenko-Tchopiwski studied the cementation of nickel by boron ; and the **boron-nickel alloys** were discussed **5**. 32, 4. A. B. du Jassonneix studied the magnetic properties of the alloys. C. Tissier obtained **nickel-aluminium alloys** by melting together aluminium and a nickel sulphide, and H. Moissan, and C. Combes prepared alloys with 20 per cent. nickel in this manner. A. Coehn and E. Tassily found that in the electrolysis of mixed soln. of aluminium and nickel sulphates, nickel free from aluminium is deposited. A. G. C. Gwyer found that the metals combine almost explosively at 1300°, and that the molten metals are completely miscible in the liquid state. F. Robin observed that the ternary alloys Al : Ni : Cu=57 : 25 : 18 have needles of the hexaluminide, a white constituent and two grey ones. L. Guillet said that the two metals form a compound *nickel hexaluminide*, $NiAl_4$, with alloys having up to 27 per cent. nickel, and with between 27 and 50 per cent. of nickel two immiscible layers are formed owing to the mutual insolubility of the two compounds $NiAl_6$ and **nickel dialuminide,** $NiAl_2$. F. R. W. Michel reported the hexaluminide to be formed by melting together aluminium and nickel chloride under a layer of a mixture of sodium and potassium chlorides, and treating the regulus with dil. hydrochloric acid. The sp. gr. of the crystal plates is 3·647, and they are completely soluble in hydrochloric acid. All the aluminium volatilizes as chloride when the aluminide is heated in hydrogen chloride. L. Guillet also reported the formation of *nickel hemialuminide*, Ni_2Al, and *nickel octitaluminide*, Ni_8Al. Only one of these statements has been verified by A. G. C. Gwyer, namely, the formation of the dialuminide. The f.p. curve has a maximum at about 1640° and 68·4 per cent. of nickel corresponding with **nickel aluminide,** NiAl, whose structure was discussed by A. J. Bradley, V. Fuss, K. Honda and T. Ishigaki, W. L. Fink and L. A. Willey, and H. Rheinboldt.

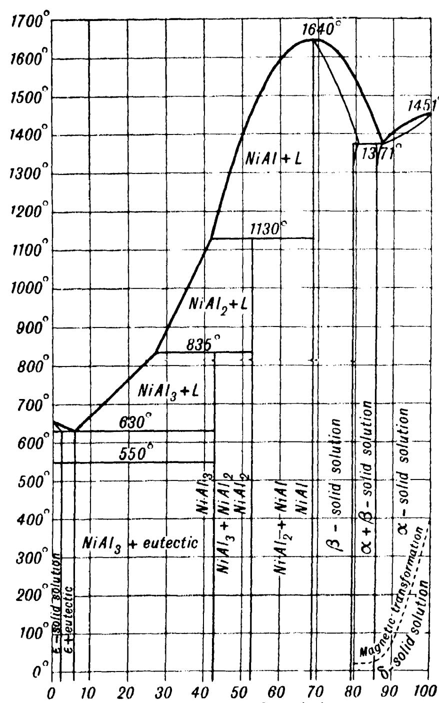


FIG. 139.—Freezing-point Diagram of the Nickel-Aluminium Alloys.

According to A. G. C. Gwyer, there is a break in the curve at about 835° and 27 per cent. of nickel; and at 1130° and 42 per cent. of nickel. There is a eutectic or rather a minimum in the curve at 1371° and 87 per cent. of nickel. In the cooling of the monaluminide, there is a reaction with the mother-liquor at 1130° resulting in the formation of the dialuminide. The eutectic at 630° and 6 per cent. of nickel represents ϵ-solid soln. and **nickel trialuminide,** $NiAl_3$. It is formed in long needles when the dialuminide reacts with the fused liquid at 830°. O. Brunck obtained this compound by treating an alloy of nickel and six times its weight of aluminium with 3 per cent. hydrochloric acid. The crystals have the colour of nickel, they have the sp. gr. 3·681, are completely soluble in hydrochloric acid, and, according to P. Groth, they are probably isomorphous with iron trialuminide, $FeAl_3$. G. Tammann and K. Dahl discussed the brittleness of the alloy at temp. up to 750°. A. G. C. Gwyer observed that two series of solid soln. are formed respectively with 68 to 81 per cent. of nickel, and with 87·5 to 100 per cent. of nickel. The limits of saturation are displaced by varying the temp. so that the alloy with 85 per cent. nickel, for example, becomes homogeneous when heated for a long time at 1030°. The alloys were also discussed by M. G. Lorentz, P. Röntgen and W. Koch, J. Asato, W. C. Devereux, A. W. Smith, E. T. Richards, N. B. Pilling and T. E. Kihlgren, J. H. Hruska, H. Schirmeister, and B. Trautmann.

A. Westgren and A. Almin observed that the lattice parameter of alloys with

Aluminium . .	0	17	22	27	38	47	54	100 atom %
a	3·519	3·546	3·557	3·569	—	—	—	— A
Volume per atom .	10·89	11·15	11·25	11·36	11·64	11·80	11·87	16·51 A^3
Contraction . .	—	7·2	8·3	10·1	12·2	14·7	16·0	—

The results were discussed by N. Steudel, W. C. Phebus and F. C. Blake, K. Becker, K. Becker and F. Ebert, and A. Westgren. H. Perlitz studied the distance apart of the atoms. G. F. Andrews observed that a 1 : 1 nickel-aluminium alloy is dull grey, porous, and brittle. H. Schirmeister found that the alloys with 12 per cent. of nickel can be rolled, but the best results were obtained with alloys with about 4 per cent. E. Ludwig found that with some binary alloys of aluminium, Brinell's hardness can be represented by $H=a+b \log P_v$, where a is a constant dependent on the nature of the added metal; b is a constant; P_v, the vol. per cent. of the compound with the added metal; and H is the depth the ball sinks expressed in μ. K. Röth observed that with nickel, where the compound $NiAl_3$ is formed, $H=624-200 \log P_v$, and

Ni .	1·0	1·5	2·0	3·0	4·0	5·0	9·8	20·0 per cent.
P_v .	0·7	1·2	1·5	2·2	3·0	3·8	7·8	15·0
H .	646	598	586	563	531	520	447	402μ

R. L. Templin and D. A. Paul measured the elastic constants, and E. Scheuer, the fluidity of the molten alloy. According to H. Schirmeister, the mechanical properties—the tensile strength in kgrms. per sq. mm., the percentage elongation, and Brinell's hardness—were found to be:

Nickel . .	0	0·6	1·0	1·9	3·1	4·5	6·2	8·1	10·3 per cent.
Tensile strength .	10·5	11·2	11·5	12·7	14·7	15·2	15·0	14·9	16·5
Elongation .	34	33	32	29	27	25	22	16	8
Hardness . .	29	—	34	—	44	—	45	47	53

E. E. McCollough studied the thermal expansion of some alloys; and H. Bohner, and W. Broniewsky, the electrical conductivity. A. G. C. Gwyer found that only the alloys with more than 85 per cent. of nickel are magnetic, and the magnetic power falls off rapidly, as illustrated by the dotted line, Fig. 139, by decreasing the proportion of nickel. The temp. at which the magnetic permeability disappears is lowered by the presence of aluminium. The transformation with nickel alone occurs at 390°, with 5, 10, and 12·5 per cent. of aluminium, it occurs at 210°, 85°, and 50° respectively. H. Betz studied the phosphorescence of the film of

oxide on the alloy; and K. Honda, and D. P. Ray-Chadhury and P. N. Sen Gupta, the magnetic properties.

Alloys with about 2 per cent. titanium were prepared by the Centralstelle für wissenschaftlichtechnische Untersuchungen; with small proportions of tin and cadmium, by H. Solbisky; with phosphorus, by F. J. Schumacher; and with magnesium, by A. L. Brooke and R. D. Mackintosh. The so-called *minckin metal* is an alloy of copper, aluminium, and nickel. L. Guillet discussed the effect of nickel on some aluminium bronzes. E. H. and A. H. Cowles and C. F. Mabery, and J. W. Richards stated that the so-called *Hercules metal* is a cupronickel with a little aluminium; and the *nickel-aluminium* of commerce is aluminium with 5 per cent. of an alloy of nickel with an excess of copper. M. Häntzschel said that one of these alloys had a sp. gr. of 2·86, a tensile strength of 13·8 kgrms. per sq. mm. and a good ring. E. Wilson found that an alloy of aluminium with 1·29 per cent. of nickel and 1·08 per cent. of copper had an elastic limit of 25·9 kgrms. per sq. mm., and at 15°, an electrical resistance of $0{\cdot}0_5341$.

Ternary **nickel-copper-aluminium alloys,** and nickel-copper-zinc alloys in which some of the zinc is replaced by aluminium have been used to some extent commercially. Alloys with over 20 per cent. of nickel and varying amounts of aluminium, have been commercialized as *aluminium-silver, minargent,* etc., as substitutes for the higher grades of nickel-silver because these alloys have a fine, silvery colour, and take a high polish. A. S. Zaimovsky and M. Frumes, D. K. Crampton and H. P. Croft, and H. Nishimura studied the nature of these alloys; and P. Merica, the precipitation hardness. G. F. Andrews found that the following Cu-Ni-Al alloys are strong, hard, and fine-grained: 66 : 24 : 10 takes a fine polish and has the colour of 10-carat gold; 55 : 33 : 12 is golden-brown; 72·5 : 21·25 : 6·25 has a rich and deep golden-brown. W. B. Parker examined the suitability of the ternary alloys for high-speed, superheated steam-turbine blades. Two commercial alloys had

Cu	Al	Ni	Mn	Zn	Fe	Si
82·07	2·54	14·64	0	0·68	trace	0·04 per cent.
79·0	11·5	5·0	0	0	4·5	— ,,

A. A. Read and R. H. Greaves prepared ternary alloys of aluminium, copper, and up to 15 per cent. of nickel. All the alloys when rolled furnished sound rods. The alloys when drawn all gave smooth sound wires. The microstructure of the alloys was studied by D. G. Jones and co-workers, V. Fuss, K. E. Bingham and J. L. Haughton, C. R. Austin and A. J. Murphy, T. S. Fuller, W. A. Mudge, J. Obata, F. Roll, W. B. Parker, and A. A. Read and R. H. Greaves. For ternary alloys with 9·70 to 10·06 per cent. aluminium, A. A. Read and R. H. Greaves found the sp. gr. to be:

Nickel . . .	0	2·46	4·95	7·48	10·14	15·75 per cent.
Sp. gr. Chill cast .	7·54	7·55	7·56	7·60	7·53	7·60
Sp. gr. Annealed .	7·54	7·54	7·63	7·57	—	—
Sp. gr. Quenched .	7·54	7·54	7·63	7·58	—	—
Sp. gr. Cold rolled .	—	7·56	7·63	7·57	—	—

and for alloys with 4·93 to 5·55 per cent. of aluminium, and

Nickel . . .	0	2·38	4·84	7·31	9·42	14·90 per cent.
Sp. gr. Chill cast .	—	8·14	8·15	8·15	8·13	8·14
Sp. gr. Annealed .	8·18	8·17	8·18	8·19	—	—
Sp. gr. Quenched .	8·18	8·16	8·18	8·18	—	—
Sp. gr. Cold rolled .	8·17	8·16	8·17	8·18	—	—

In spite of the fact that the sp. gr. of nickel, 8·80, is less than that of copper, 8·93, the presence of nickel raises the sp. gr. This is most marked with the alloy containing 10 per cent. of aluminium, and 5 per cent. of nickel. In this series, with larger amounts of nickel, the sp. gr. falls in spite of a slight decrease in the proportion of aluminium. The slow cooling of the alloys increases the sp. gr. so that

in alloys with 5 per cent. of aluminium, and 5 and 7·5 per cent. of nickel, the respective sp. gr. in the annealed states are 8·178 and 8·192, and in the quenched states 8·176 and 8·180. These data correspond with the respective decreases in vol. of 0·2 part per 1000 and 1·5 parts per 1000 respectively on slow cooling.

A. A. Read and R. H. Greaves measured the scleroscope hardness, and Brinell's hardness; for the latter a 10 mm. ball under a load of 3000 kgrms. applied for 1 min. was used for the alloys with 10 per cent. aluminium,

Nickel	. . .	0	1·04	2·46	4·98	7·48	10·14	15·75 per cent.
Scleroscope	Chill cast .	20·0	33·0	36·5	41·0	35·0	35·0	32·0
	Annealed .	20·5	22·0	27·0	25·0	26·0	28·0	—
	Quenched.	62·0	56·0	49·0	53·0	40·0	45·0	45·0
	Cold rolled	33·0	39·0	38·0	40·0	43·0	—	—
Brinell's	Chill cast .	135	150	176	199	179	182	182
	Annealed .	127	139	158	151	162	173	—
	Quenched.	257	211	206	251	209	214	205
	Cold rolled	186	214	207	216	231	—	—

and for alloys with 5 per cent. of aluminium, the load in Brinell's test was 1000 kgrms.:

Nickel	. . .	0	0·94	2·38	4·84	7·31	9·42	14·90 per cent.
Scleroscope	Chill cast .	9·0	10·5	11·0	12·0	13·5	17·0	37·0
	Annealed .	8·5	10·5	11·0	12·5	27·0	—	—
	Quenched.	11·0	11·0	11·5	12·0	17·0	—	—
	Cold rolled	17·0	18·5	21·0	23·0	27·5	—	—
Brinell's	Chill cast .	58	59	59	60	77	115	173
	Annealed .	61	64	66	80	167	—	—
	Quenched.	52	56	62	61	92	—	—
	Cold rolled	114	113	124	136	156	—	—

The effect of cold-rolling, and especially of quenching, is greater in proportion with the scleroscope hardness than it is with Brinell's hardness—Figs. 140 and 141. There is a rapid increase in the hardness of the 5 per cent. aluminium alloys in the annealed state in the presence of over 5 per cent. of nickel, and in the cast state with over 7·5 per cent. of nickel. The increase is so rapid that when the proportion of nickel reaches 7·5 per cent., the annealed metal with 5 per cent. of aluminium is harder than the corresponding alloy with 10 per cent. aluminium; similarly with the cast metal having 15 per cent. nickel. The hardening capacity of the alloys—shown by the ratio of the hardness in the quenched state to that in the annealed state—increases as the proportion of nickel increases, but there is in general a marked and regular decrease in the hardening capacity in the alloys with 10 per cent. aluminium. The ratio in the alloys with 5 per cent. of aluminium falls below unity when the nickel reaches 5 per cent. and is still further reduced when the nickel attains 7·5 per cent. This shows that the alloys are considerably softened by quenching.

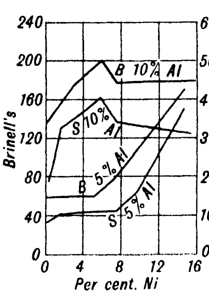


FIG. 140.—Hardness of Chill Castings.

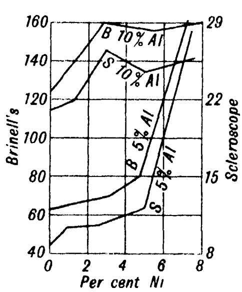


FIG. 141.—Hardness of Annealed Rods.

W. B. Parker found that the mechanical properties of alloys:

Cu : Ni : Al	Modulus of elasticity (lbs. per sq. in.)	Yield-point (tons per sq. in.)	Maximum load (tons per sq. in.)	Elongation on 2 inches (per cent.)	Reduction of area (per cent.)
82·07 : 14·64 : 2·54	21,150,000	30·5	57·0	10·0	13·0
79·63 : 4·13 : 9·77 .	17,055,010	15·0	45·0	12·0	16·0
79·0 : 5·0 : 11·5 .	18,500,000	18·0	58·0	8·0	11·0

H. Tomlinson found Young's modulus of nickel-silver to be 1335×10^6 grms. per sq. cm.; the torsional rigidity, $493 \cdot 7 \times 10^6$ grms. per sq. cm.; and Poisson's ratio, 0·354. F. C. Lea, H. J. French and W. A. Tucker, W. Rosenheim, and S. L. Archbutt and co-workers also studied the mechanical properties of these alloys.

A. A. Read and R. H. Greaves reported that the mechanical tests for chill castings, expressed in tons per sq. in., were

Nickel	. . . . .	0	0·96	5·18	10·14	14·62	per cent.
10 per cent. Al	Yield-point .	11·6	12·8	19·9	25·1	16·5	
	Maximum stress .	30·43	35·50	39·80	38·48	29·18	
	Elongation (2 ins.)	19·4	20·2	7·2	2·8	3·2	,,
	Reduction area .	27·2	21·5	10·1	4·6	5·5	,,
Nickel	. . . . .	0	1·00	5·05	9·42	14·90	,,
5 per cent. Al	Yield-point .	5·0	5·5	5·6	15·42	35·1	
	Maximum stress .	18·73	19·26	18·67	28·27	41·56	
	Elongation (2 ins.)	68·0	92·1	86·5	39·7	4·7	,,
	Reduction area .	58·2	69·1	73·1	39·0	10·0	,,

The results are plotted in Fig. 142. The results with rolled and annealed rods, plotted in Fig. 143, are:

Nickel	. . . . .	0	2·46	4·95	7·48	—	per cent.
10 per cent. Al	Yield-point .	14·4	18·1	18·0	18·8	—	
	Maximum stress .	25·68	31·88	35·56	38·91	—	
	Elongation (2 ins.)	9·0	12·3	16·2	13·1	—	,,
	Reduction area .	10·4	13·0	17·4	15·1	—	,,
Nickel	. . . . .	0	0·94	2·38	4·84	7·31	,,
5 per cent. Al	Yield-point .	5·2	5·3	5·5	9·4	24·0	
	Maximum stress .	22·16	23·78	22·86	25·86	39·00	
	Elongation (2 ins.)	82·5	94·6	90·2	70·0	25·6	,,
	Reduction area .	78·9	76·1	71·0	60·2	26·8	,,

The mechanical tests on cold-rolled rods gave:

Nickel	. . . . .	0	2·46	4·95	7·48	—	per cent.
10 per cent. Al	Yield-point .	42·0	36·9	40·2	47·8	—	
	Maximum stress .	44·28	51·24	51·40	52·01	—	
	Elongation (2 ins.)	9·0	13·0	12·1	12·3	—	,,
	Reduction area .	12·4	11·0	8·4	16·3	—	,,
Nickel	. . . . .	0	0·94	2·38	4·84	7·31	,,
5 per cent. Al	Yield-point .	17·4	18·1	22·5	23·5	31·1	
	Maximum stress .	27·20	28·18	30·12	31·11	36·30	
	Elongation (2 ins.)	64·0	63·1	55·0	50·0	28·8	,,
	Reduction . .	75·1	78·1	66·7	72·3	41·0	,,

and similarly, with quenched rods,

Nickel	. . . . .	0	2·46	4·95	7·48	—	per cent.
10 per cent. Al	Yield-point .	35·0	—	18·0	20·0	—	
	Maximum stress .	53·55	45·34	46·56	49·58	—	
	Elongation (2 ins.)	2·3	5·4	4·2	6·3	—	,,
	Reduction area .	3·9	5·4	5·5	5·5	—	,,
Nickel	. . . . .	0	0·94	2·38	4·84	7·31	,,
5 per cent. Al	Yield point .	6·4	6·6	7·2	7·6	11·4	
	Maximum stress .	22·79	22·83	24·85	24·22	29·77	
	Elongation (2 ins.)	78·6	85·6	77·8	86·8	52·1	,,
	Reduction area .	73·3	73·8	41·4	72·4	65·1	,,

In the alloys with 10 per cent. aluminium, the increase in the maximum stress and yield-point of the chill castings is obtained up to 10 per cent. nickel at the expense of elongation and reduction of area; the mechanical properties of the annealed rods are improved by the addition of 5 per cent. of nickel. The only change in the cold-rolled rods with increasing proportions of nickel is a rise in the maximum stress without a decrease in ductility. A comparison of the mechanical properties of quenched and annealed alloys shows that the increase in maximum stress, due to quenching, decreases as the percentage of nickel rises. The effect of quenching is to reduce slightly the maximum stress; the elongation and reduction

of area increase with the proportion of nickel, but they are very small throughout. The yield-points of the quenched alloys are not well defined, and their elastic behaviour was examined in the extensometer:

With alloys having 10 per cent. of aluminium and 0, 4·95, and 7·48 per cent. of nickel, the limit of proportionality of stress to strain was reached in each case at a stress of approximately 8 tons per sq. in. The increments of strain corresponding to successive equal increments of stress then increased continually, accompanied by a perceptible amount of permanent set. In the case of the alloy with 7·48 per cent. of nickel a very decisive "creeping point" was reached at a stress of 20 tons per sq. in. In the case of the alloy with 4·95 per cent. of nickel a somewhat less marked creeping point was reached at a stress of 18 tons per sq. in. In the case of the alloy with no nickel, although the limit of proportionality was no higher than in the alloy with 4·95 or 7·48 per cent. of nickel, that is, about 8 tons per sq. in., no definite evidence of creeping was detected until the stress reached an intensity of 35 tons per sq. in. The total amount of creep which occurred at this load did not exceed $\frac{1}{10,000}$ inch, and a self-hardening action then set in which enabled the stress to be raised to 47 tons per sq. in. before pronounced creeping was resumed.

In the alloys with 5 per cent. of aluminium, the addition of up to 5 per cent. of nickel improves the elongation and reduction of area without affecting the yield-point and the maximum stress; but with over 5 per cent. of nickel, the latter properties are improved but the elongation and reduction of area suffer a corresponding decrease. With the annealed rods, the maximum stress and yield-point rise slowly with increasing proportions of nickel, up to 5 per cent., after which, up to 7·5 per cent., the increase is rapid. With cold-rolled rods, the maximum stress and yield-point are raised whilst the elongation and reduction of area decrease slowly with between 1 and 5 per cent. of nickel, and more quickly with over 5 per cent. of nickel. With quenched rods, the effect of increasing the nickel up to 5 per cent. is to increase slightly the yield-point and maximum stress, and improve the ductility; but with over 5 per cent. of nickel, the increase in the yield-point and maximum stress is more rapid, and there is a corresponding fall in the elongation and reduction of area. Comparing the results for the quenched and annealed rods, with less than 5 per cent. of nickel, the maximum stress is scarcely affected by quenching, though the yield-point is slightly raised, and the elongation and reduction of area are diminished. With 5 per cent. nickel, the ductility is increased by quenching, while the maximum stress and yield-point are lowered. This effect is marked with 7·5 per cent. nickel.

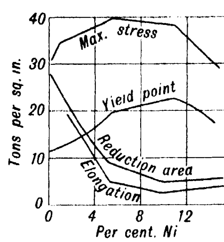


FIG. 142.—Tensile Tests—Chill Castings with 10 per cent. Al.

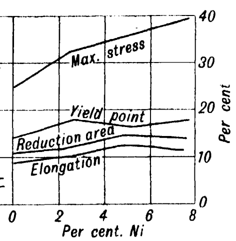


FIG. 143.—Tensile Tests—Rolled and Annealed with 10 per cent. Al.

The mechanical properties of air-cooled alloys are:

	10 per cent. Al		5 per cent. Al	
Nickel	4·95	7·48	4·84	7·31 per cent.
Yield-point	18·1	17·0	7·6	11·6
Maximum stress	41·76	42·64	23·79	27·06
Elongation (2 ins.)	12·9	15·2	81·0	63·9 ,,
Reduction of area	10·0	14·1	68·7	69·9 ,,

Hence, the mechanical properties of air-cooled alloys with 5 per cent. aluminium and upwards of 5 per cent. nickel approximate to those of the quenched rather than those of the annealed metal. The maximum stress is even slightly lower than that of the quenched material, probably owing to the absence of any hardening effect by strains set up in quenching. T. Saito, S. F. Herman and F. T. Sisco, I. Iitaka, and L. J. Wood and S. W. Parr studied the mechanical properties of the nickel-aluminium-copper alloys.

A. A. Read and R. H. Greaves found that the alternating stress tests gave for the number of alternations resisted :

Nickel		0	2·46	4·95	7·48	— per cent.
10 per cent. Al	Annealed	38	57	147	54	—
	Cold rolled	231	165	145	511	—
	Quenched	← irregular →				
Nickel		0	0·94	2·38	4·84	7·31 ,,
5 per cent. Al	Annealed	741	746	671	445	193
	Cold rolled	773	580	354	229	150
	Quenched	1045	862	738	400	258

The resistance of cold-rolled rods to alternating stresses is reduced by the presence of nickel; and the detrimental effect of annealing the 10 per cent. aluminium alloys is to some extent diminished by 5 per cent. of nickel. The results for quenched rods are unreliable. In the alloys with 5 per cent. of aluminium, an increasing proportion of nickel reduces the resistance to alternating stress; but in the annealed state there is no decrease until the proportion of nickel exceeds 1 per cent. The effect of quenching is to increase the resistance of the alloys to alternating stresses.

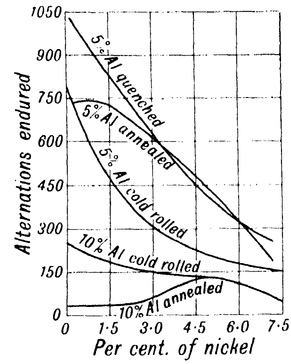


FIG. 144.—The Effect of Nickel on the Alternating Stress Test.

F. Roll observed a break in the dilation curves of some of the alloys indicating an unknown transformation. E. Griffiths and F. H. Schofield, and G. A. Shakespear measured the thermal conductivities of some of the light alloys. A. A. Read and R. H. Greaves, and C. R. Austin and A. J. Murphy measured the m.p. of alloys with 10 per cent. of aluminium, and found for

Nickel	0	2·46	5·18	7·48	10·14	14·62 per cent.
M.p.	1042°	1039°	1042°	1053°	1079°	1063°

There is thus a slight fall followed by a rise before the nickel reaches 5 per cent.; whilst with the 5 per cent. aluminium alloys there is an immediate rise in the m.p. of the alloys :

Nickel	0	2·38	5·05	7·31	9·42	14·90 per cent.
M.p.	1054°	1081°	1093°	1097°	1108°	1119°

A. A. Read and R. H. Greaves found that the sp. electrical resistance R microhms—or ohms$\times 10^{-6}$—and the relative conductivity (copper 100) of the ternary alloys are as follows :

	Al 10 per cent.			Al 5 per cent.				
Nickel	0	1·04	2·46	0	0·94	2·38	4·84	7·31 per cent.
R	10·27	11·74	14·40	9·85	10·88	12·56	15·47	18·45
Conductivity	16·0	14·0	11·4	16·7	15·1	13·1	10·6	8·9

The results for the conductivity are plotted in Fig. 145. The conductivity for the alloy with 5 per cent. of aluminium is slightly greater than for alloys with 10 per cent. of aluminium. In both cases, the conductivity is diminished by the addition of increasing proportions of nickel. The effects of quenching, air cooling, and annealing with slow cooling of alloys with 5 per cent. of aluminium, are as follow :

	$R\times 10^{-6}$ ohm			Conductivity (Cu=100)		
	Annealed	Air-cooled	Quenched	Annealed	Air-cooled	Quenched
Nickel 4·84 per cent.	15·49	14·47	15·54	10·6	10·6	10·6
Nickel 7·31 ,,	18·01	18·45	18·43	9·15	8·93	8·94

Slow cooling increases the electrical conductivity of the alloys. The resistance of the alloy with 7·5 per cent. of nickel is lowered by annealing and slow cooling,

whilst the quenched material has nearly the same value as that of the air-cooled material. H. Tomlinson found that the increase of resistance per unit produced by a stress of a gram per sq. cm. is 2346×10^{-12}; the increase of resistance per unit of sp. resistance which would be caused by a stress sufficient to double the length of the wire, 0·226. E. F. Northrup measured the resistance of aluminium-magnesium-nickel (90 : 8 : 2) alloys. A. Schulze also studied the electrical resistance of these alloys. O. L. Kowalke observed the thermoelectric force of couples of aluminium-nickel alloys against iron, and nichrome—*vide infra*, Fig. 159, and W. Rohn, against platinum; J. Obata studied the Hall effect; E. C. Stoner, and J. Cournot studied the non-magnetic alloys of the two elements; A. Kussmann and B. Scharnoff observed no relation between the coercive force and hardness.

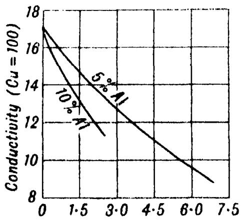


FIG. 145.—The Effect of Nickel on the Conductivity of Cu-Al-Ni Alloys.

F. Roll found that alloys with nickel 3·5 to 5·5 per cent.; aluminium, 46 to 50; and copper, 46·50, fell to a fine powder on exposure to air. A. A. Read and R. H. Greaves observed that alloys containing up to 10 per cent. of nickel resist corrosion by sea-water and alkaline soln. better than aluminium-copper alloys, but the latter resist attack by acids better than alloys containing nickel. They found for soft tap-water, and for sea-water, the following losses in weight in lbs. per sq. ft. per month :

	Nickel per cent.	Sea-water Annealed	Sea-water Cold-rolled	Tap-water Annealed	Tap-water Cold-rolled
10 per cent. Al	0·00	0·00091	0·00059	0·00009	0·00008
	0·97	0·00022	0·00024	0·00006	0·00009
	4·94	0·00012	0·00013	0·00011	0·00012
	9·98	0·00009	0·00001	0·00009	0·00008
5 per cent. Al	0·00	0·00031	0·00034	0·00006	0·00006
	0·92	0·00031	0·00031	0·00008	0·00008
	4·90	0·00012	0·00012	0·00007	0·00009
	10·07	0·00005	0·00002	0·00012	0·00012
1 per cent. Al	0·00	0·00244	0·00211	0·00011	0·00010
	1·03	0·00221	0·00214	0·00010	0·00013
	3·57	0·00106	0·00163	0·00015	0·00012
	9·83	0·00018	0·00015	0·00011	0·00010
Muntz metal		0·00158	0·00143	0·00040	0·00033
Naval brass		0·00140	0·00131	0·00020	0·00022

The results for sea-water are plotted in Fig. 146. In all cases, the effect of nickel up to 10 per cent. is greatly to reduce the corrosion of alloys by sea-water, and the effect of the first 1 per cent. of nickel on the 10 per cent. aluminium alloy is very marked. The cold-rolled and annealed alloys behave similarly. Again, the corrosion with some acids and dil. soda-lye was found to be :

	10 per cent. Al			5 per cent. Al		
Nickel	0	4·95	7·48	0	4·84	7·31 per cent.
$0{\cdot}1N$-NaOH	0·00022	0·00018	0·00019	0·00042	0·00026	0·00023
Vinegar	0·0004	0·00090	0·00089	0·00075	0·00060	0·0104
$0{\cdot}1N$-H_2SO_4	0·0015	0·0036	0·0142	0·0060	0·0062	0·0058
$0{\cdot}1N$-HCl	0·0016	0·0406	0·0374	0·039	0·035	0·036

Observations were made by G. M. Enos, and T. Saito. The rate of corrosion by $0{\cdot}1N$-NaOH is very small and is diminished by the presence of nickel though not so greatly as with sea-water. The presence of nickel greatly increases the corrosion by vinegar, especially in the 10 per cent. aluminium series of alloys. The rate of corrosion by $0{\cdot}1N$-H_2SO_4 is also greatly increased by nickel in the 10 per cent. aluminium series, but is almost unaffected by nickel in the 5 per cent. aluminium series. The corrosion with $0{\cdot}1N$-HCl is very great; the 10 per cent. aluminium alloy without nickel withstood the action best. The rate of corrosion

of the 5 per cent. aluminium alloys is not affected by the presence of nickel, but the corrosion of the alloy with 10 per cent. of aluminium is greatly increased as the proportion of nickel increases. The subject was studied by A. von Zeerleder, and P. Renaud. H. Gruber found the increase in weight when plates 60×13×12 mm. were exposed for an hour to hydrogen sulphide, to be :

	Ni : Al	700°	800°	900°	1000°
Gain in weight	100 : 0	9·67	35·0	—	—
	95 : 5	4·39	14·7	17·0	25·0
	90 : 10	0·29	1·26	2·78	10·0
	85 : 15	0·04	0·25	0·90	1·17

L. Nathan observed that German silver vessels are inclined to check the fermentation of apples, and beer-work. K. E. Bingham and J. L. Haughton, W. A. Mudge, L. J. Wood, T. S. Fuller, and A. A. Read and R. H. Greaves studied the **copper-aluminium-nickel alloys**—*vide supra ;* and R. K. Hezlet and R. Genders, **silver-aluminium-nickel alloys.** V. Fuss, S. Hashimoto, and W. Rosenhain and co-workers studied some **aluminium-magnesium-nickel alloys,** and some **aluminium-zinc-nickel alloys ;** S. Daniels, some **aluminium-magnesium-nickel-copper alloys ;** and C. Hisatsune, some **aluminium-silicon-nickel alloys.** W. A. Wesley and co-workers noted the action of hot aerated milk on the alloy.

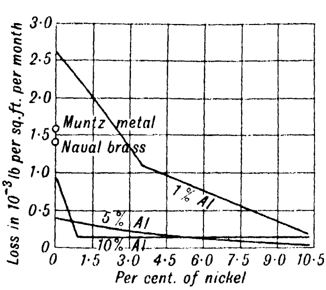


FIG. 146.—The Corrosion of Aluminium-Nickel Alloys by Sea-Water.

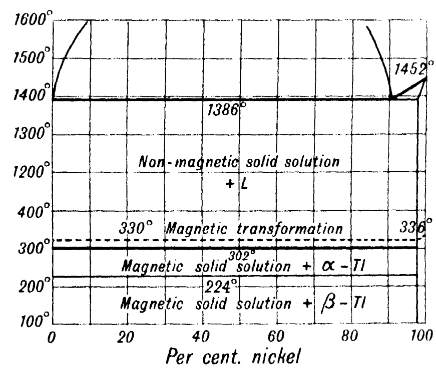


FIG. 147.—The Freezing-point Curves of the Nickel-Thallium Alloys.

L. J. Wood and S. W. Parr studied the resistance of the nickel-aluminium-copper alloys to corrosion ; L. Nowack, the age-hardening of the **gold-aluminium-nickel alloys.**

M. Dubowicky[11] studied the cementation of nickel by silicon. The **nickel-silicon alloys** were studied by O. Dahl and co-workers, J. T. Littleton, and A. L. Marsh—*vide* silicon. G. Masing, E. Crepaz, L. Guillet and co-workers, A. Schulze, and J. Arnott studied the age-hardening of the copper-nickel-silicon alloys ; D. G. Jones and co-workers, their mechanical properties ; M. G. Corson, their structure ; L. Nowack, the age-hardening of the **gold-nickel-silicon alloys ;** B. E. Field, the acid-resisting qualities of the **nickel-aluminium silicon alloys ;** W. Rohn, the thermoelectric force of the nickel-titanium alloys against platinum ; M. Guillet and co-workers, and C. L. Wilson and co-workers, the **copper-nickel-silicon alloys**; and W. Rosenhain and co-workers, O. Dahl, and F. C. Lea, the mechanical properties of the **copper-nickel-magnesium-aluminium alloys.**

W. Kroll studied some **gallium-nickel alloys.** G. Voss investigated the **nickel-thallium alloys** and observed that the fused metals are not miscible between 0° and 90 per cent. of nickel. Nickel retains 3 per cent. of thallium in solid soln., and the solid soln. is in equilibrium at 1386° with two liquid layers, Fig. 147. The transition temp. of non-magnetic to magnetic nickel is lowered by enough thallium to form a sat. solid soln. and remains constant on further addition.

The nickel-silicon alloys were discussed in connection with silicon—**6**. 13, 40. Observations were also made by O. Dahl and N. Schwartz, M. Dubowicky, R. Walter, and B. Borén. M. A. Hunter and J. W. Bacon, O. Lane, and R. Franks and B. E. Field studied the magnetic properties of the **nickel-titanium alloys**; A. Schulze, the electrical conductivity, and M. A. Hunter and J. W. Bacon, the magnetic properties of the **copper-nickel-titanium alloys**; and R. Franks and B. E. Field, and K. Grassman and E. J. Kohlmeyer, **nickel-zirconium alloys.** The trade term *cooperite* applies to a **nickel-zirconium alloy** (Ni, 80; Sb, 14; Zr, 6) which is said to be very strong and suitable for the cutting tools. N. Petinot made alloys of the two elements in an electric furnace. T. E. Allibone and C. Sykes measured the sp. resistance, and magnetic induction of some nickel-zirconium alloys. E. Chauvenet[12] prepared a **nickel-thorium alloy,** which he considered to be nickel dithoride, $NiTh_2$, by reducing potassium thorium chloride, or thorium chloride with lithium in a nickel boat. The alloy furnishes grey lamellæ, or else a black, pyrophoric powder contaminated with about 10 per cent. of thoria. The pyrophoric variety inflames spontaneously when powdered in a mortar, or when dried at 115°. It does not form nickel carbonyl when heated to 60° in a current of carbon monoxide, but at 400°, the gas is decomposed with the deposition of carbon. The alloy is non-magnetic; it is rapidly dissolved by hydrochloric acid. K. Grassmann and E. J. Kohlmeyer examined the **nickel-cerium alloys.**

A. F. Cronstedt,[13] T. Bergman, and A. and C. R. Aikin described some **nickel-tin alloys,** which were found to be white, hard, and brittle. T. Fleitmann observed that nickel alloys with up to 10 per cent. of tin without losing its working qualities. Alloys were studied by D. J. Reisz and co-workers, and J. Cournot. L. Guillet investigated the cementation of nickel by tin. C. T. Heycock and F. H. Neville observed that the addition of one atomic per cent. of nickel to tin lowered the m.p. of the latter 2·94°. H. Gautier measured the m.p. of these alloys and obtained a maximum on the curve at 1310° and 43 per cent. of nickel corresponding with **nickel ditritastannide,** Ni_3Sn_2—*vide infra*—as well as two eutectics, one at 231° and 0·01 per cent. of nickel, and the other at 1160° and 70 per cent. of nickel. G. Charpy also observed minima with 2 and 60 per cent. of nickel, and a maximum with 43 per cent. According to L. Guillet, nickel and tin can form four solid soln.—(i) a magnetic α-solid soln. with 0 to 5 per cent. of tin; (ii) a non-magnetic α-solid soln. with 0 to 5 per cent. of tin; (iii) a β-solid soln. with 38 to 41 per cent. of tin; and (iv) a γ-solid soln. with 55 to 60 per cent. of tin—and one compound, nickel stannide, NiSn, in crystals large enough to be seen by the naked eye. Alloys with 5 to 38 per cent. of tin consist of the α-solid soln., or of the β-solid, and the α-β eutectic; those with 41 to 55 per cent. of tin consist of β- and γ-solid soln.; those with 60 to 67 per cent. of tin contain the γ-solid soln. and the monostannide; and finally, those with 65 to 100 per cent. of tin contain the monostannide or the Sn-α-solid soln. eutectic.

G. Voss studied the equilibrium conditions of the alloys, and his results are summarized in Fig. 148. The alloys with 3·5 to 18 and 26 to 45 per cent. of nickel separate into two layers. There are no definite maxima on the f.p. curve, but there are three breaks, and a eutectic at 1135° and 68·5 per cent. of nickel, and another at 229° and 1·3 per cent. of nickel. Between 30 and 45 per cent. of nickel, the two liquid layers react at 1235° to form the ditritastannide. A break on the cooling curve at 1162° corresponds with the formation of **nickel tritastannide,** Ni_3Sn—*vide infra*—in long needles from a reaction between the ditritastannide and a fused mass with 65 per cent. of nickel. With alloys having 60 to 85 per cent. of nickel, there is a break in the cooling curve at 855° due to a reaction between the tritastannide and the solid soln. resulting in the formation of **nickel tetritastannide,** Ni_4Sn. With alloys having 42·5 to 60 per cent. of nickel, there is a slight thermal effect at 837°—may be lower if supercooling occurs—and it is taken to represent the breaking down of the tritastannide into the ditritastannide

and the tetritastannide. Only one series of solid soln. with 0 to 15 per cent. of tin was observed by G. Voss. A. S. Russell and co-workers examined the compounds formed in mercury soln. The properties of the alloys were studied by E. M. Wise and J. T. Eash, E. S. Hedges and C. E. Homer, and A. W. Smith; and their sp. ht., by P. Schübel.

L. Guillet found that the alloys formed of α-solid soln., and those formed of the Sn-γ-solid soln. are ductile, and possess the mechanical properties of nickel or tin; all the others except those containing more than 90 per cent. of tin are extremely hard or fragile, the α-solid soln. being the most fragile. E. Vigouroux observed that the alloys with 13·64, and 83·65 per cent. of tin are hard, brittle, and grey; whilst the alloy with 92·71 per cent. of tin is bluish-white and malleable. Only the first of these three alloys is sonorous. The sonorous alloys contain 66·76 to 85 per cent. of tin; the fragility of the alloys increases with the proportion of tin up to 66·76 per cent., and then diminishes so that alloys with 85 to 100 per cent. of tin are somewhat malleable.

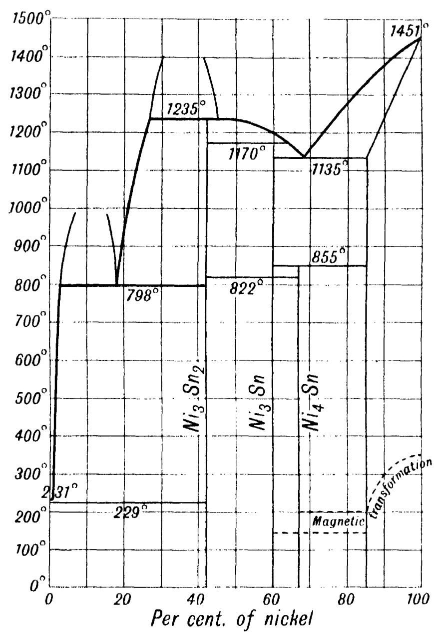


FIG. 148.—Freezing-point Curves of the Nickel-Tin Alloys.

According to E. Vigouroux, when the alloys with 13·64, 83·65, and 92·71 per cent. of tin are treated alternately with warm nitric acid and fused potassium hydroxide, a residue of **nickel stannide,** NiSn, remains as a silver-white, non-magnetic, crystalline powder of sp. gr. 8·44 at 0°/0°. The calculated sp. gr. is 7·93. I. Oftedal gave for the dimensions of the hexagonal cells of nickel monostannide, NiSn, c=5·174 A., a=4·081 A., or $a:c$=1·268. According to E. Vigouroux, the monostannide is attacked by chlorine at a red-heat, with the formation of chlorides of the two metals; it burns with incandescence in oxygen; sulphur vapour converts it into the sulphides of the two metals; hydrochloric acid, sulphuric acid, and aqua regia dissolve it completely, but nitric acid has little effect even after a prolonged boiling; fused alkali hydroxides, carbonates, and nitrates attack it but slowly, though potassium chlorate oxidizes it below its m.p. The monostannide may be a solid soln., a eutectic alloy, or a mixture of isomorphous forms, but it is considered certain that it is not a mixture of the free metals since a mixture of the powdered metals behaves quite differently from the supposed monostannide.

E. R. Jette and E. Fetz studied the X-radiograms, and the hardness of the alloys. W. Meissner and co-workers studied the resistance at very low temp. N. A. Puschin found that the e.m.f., E millivolts, of the alloys in soln. of stannous chloride,—Sn : $SnCl_2$: $SnNi_n$, E_1—N-H_2SO_4—Sn : N-H_2SO_4 : $SnNi_n$, E_2—and N-KOH—Sn : N-KOH : $SnNi_n$, E_3 are:

Nickel, n .	12	20	34	45	55·2	63	75	87	100 at. per cent.
E_1 . .	0	0	0	2	280	280	216	196	222
E_2 . .	−6	−1	0	6	370	360	260	280	382
E_3 . .	2	13	27	29	370	440	500	448	465

There is an abrupt change in all cases with alloys having 50 at. per cent. of nickel; and this is in agreement with the assumed existence of a monostannide; there is

no evidence of a *nickel hemistannide*, Ni_2Sn. A. Battelli observed that the thermoelectric force of nickel-tin alloys against lead is greater than that calculated from the mixture rule, so that it exceeds the value for tin alone.

T. J. Seebeck observed that some of the nickel-tin alloys are magnetic. K. Honda, E. C. Stoner, and J. Cournot studied the magnetic properties of alloys of the two elements. L. Guillet observed that only alloys with less than 38 per cent. of tin are magnetic at ordinary temp., and possess transformation points representing the change to the non-magnetic state, and they all contain the α-solid soln. or eutectic, and this is the sole magnetic constituent of these alloys. E. Vigouroux said that the magnetic alloys contain 0 to 40·22 per cent. of tin. G. Voss added that only alloys with up to 60 per cent. of nickel are magnetic. The temp. at which the magnetic property disappears on heating falls from 350° for pure nickel to 145° for alloys with 62 per cent. of that metal. The fall is from 190° to 130°, *i.e.*, 60° for alloys with 67 to 65 per cent. of nickel corresponding with the disappearance of the solid soln. The loss of magnetic power on heating and its return on cooling occur at:

Nickel	100	95	90	80	70	67	65	62 per cent.
Loss on heating . .	350°	330°	325°	195°	195°	192°	140°	145°
Restoration on cooling .	325°	300°	280°	180°	180°	185°	120°	115°

B. V. Hill found that with 0, 5, 10, and 15 per cent. of tin, the transformation temp. occurred at 340°, 303°, 268°, and 230° respectively.

E. Vigouroux observed that whilst the nickel-tin alloys are dissolved by hydrochloric and sulphuric acids, nitric acid disintegrates them, producing nickel and metastannic acid, and with an alloy containing 92·71 per cent. of tin, a little nickel is dissolved. When the alloys with 13·64, 83·65, and 92·71 per cent. of tin are treated alternately with warm nitric acid and fused alkali hydroxide, the monostannide remains as a residue, whilst alloys with 9·01, 22·74, 35·05, and 37·50 per cent. of tin, when similarly treated, furnish the tritastannide as a light brown, non-magnetic, crystalline powder of sp. gr. 8·98 at 0°/0°—the calculated value is 8·17. It is soluble in molten nickel; it is attacked by oxygen at a red-heat, and by chlorine with incandescence; hydrochloric acid attacks it at ordinary temp. and dissolves it completely on warming; sulphuric acid, and aqua regia dissolve it more quickly; and dil. nitric acid has little action even when warm, but the conc. acid produces metastannic acid. When alloys with 45 to 57 per cent. of tin are treated alternately with nitric acid and alkali hydroxide, the ditritastannide remains. The action of hydrochloric acid on alloys with 59 to 66 per cent. of tin diminishes the proportion of tin towards the minimum 57·47 per cent. corresponding with Ni_3Sn_2, whilst nitric acid raises it towards a maximum of 66·97 per cent. corresponding with NiSn.

The ternary **copper-nickel-tin alloys** can be obtained by melting together the constituent metals as was done by C. Bischof, and L. Elsner. The latter obtained the 2 : 1 : 1-alloy and found its sp. gr. to be 8·948, and observed that it is not attacked by air or by hydrogen sulphide. C. Langbein obtained the ternary alloys by the electrolysis of a soln. of the metal phosphate in a soln. of sodium pyrophosphate. The alloy *adnic*, described by W. B. Price, has copper 70, nickel 29, and tin 1. W. B. Price and co-workers, and J. Veszelka discussed the equilibrium diagram. D. J. McAdam gave the following static mechanical tests, and the fatigue tests of an annealed Cu : Ni : Sn (69·82 : 29·08 : 0·95) alloy, expressed in lbs. per sq. in.: Tensile strength, 87,300; torsional strength, 48,000; shearing strength, 50,900; elastic modulus, $21{\cdot}4\times10^6$; and endurance limit, 22,500. The subject was discussed by J. T. Eash and C. Upthegrove, W. C. Ellis and E. E. Schumacher, E. Fetz, W. H. Finkeldey, L. Guillet and co-workers, R. Ozleberger, and C. Upthegrove and co-workers. J. Webster observed the effect of additions of *aluminium*; and of *bismuth* on these alloys. The Cu-Ni-Sn-Bi-Al alloys are elastic, and are not readily oxidized. The effect of adding *zinc* to the copper-nickel-tin alloys was observed by C. Diegel, and C. Keferstein. The *Suhler Weisskupfer* has

Cu, 40·4 ; Ni, 25·4 ; Sn, 2·6 ; and Zn, 25·4. E. Grüneisen found that the old alloy *Rotgass* with its Cu, 85·7 ; Ni, 6·39 ; Sn, 6·39 ; and Zn, 7·15, has a modulus of elasticity of 8244 kgrms. per sq. mm. V. Schmidt, and R. B. Wheatley observed the effect of manganese on the quaternary alloy ; M. Ashbarium, the effect of manganese ; and J. Webster, the effect of bismuth. J. McNeill discussed the *nickel bronzes.* Sauvage's alloy *neogen* contains Cu, 58 ; Ni, 12 ; Sn, 2 ; Zn, 0·5 ; Bi, 0·5 ; and Al, 0·5. The alloy Ni, 40 ; Ag, 10 ; Al, 30 ; Sn, 10 has the trade-name *rosein ;* it is used for jewelry. The alloy Cu, 70 ; Ni, 29 ; Sn, 1 was called *admiralty nickel,* or *adnic.* It is a corrosion-resisting and heat-resisting alloy described by W. B. Price. P. Hidnert and W. T. Sweeney obtained for the mean coeff. of thermal expansion, α,

	20° to 100°	100° to 200°	200° to 300°	20° to 200°	20° to 300°
$\alpha \times 10^6$ . .	15·2	15·5	18·0	15·4	16·3

The alloy Cu, 64 ; Ni, 35 ; Sn, 1 was called *newloy ;* and *barberite,* 85, Cu ; 5, Ni ; 5, Sn ; and 5, $SiCu_x$. W. B. Price and co-workers found that a number of these ternary alloys could be hardened by heat treatment. Thus, the alloy with Cu, 64·4 ; Ni, 27·6 ; Sn, 8, had the Brinell's hardness 114 when cast ; 100, when homogenized and quenched ; 196, when homogenized and furnace cooled ; 114, when homogenized and air-cooled ; 228, when homogenized and drawn at 400° ; 321, when homogenized and drawn at 500° ; and 179, when homogenized and drawn at 500°. C. G. Fink and C. M. Decroly studied the corrodibility of barberite in sulphuric acid ; and R. Nitzsche, that of the nickel bronzes. The alloys were studied by E. M. Staples and co-workers, F. Orme, F. Delarozière, and N. B. Pilling and T. E. Kihlgren. M. Ballay, and L. Guillet and co-workers studied the **copper-nickel-tin-silicon alloys.** E. Griffiths and F. H. Schofield studied the thermal and electrical conductivities of some aluminium bronzes containing nickel ; and T. Ishikawa, the hardness of these alloys. S. Kato investigated the **nickel-tin-aluminium alloys.**

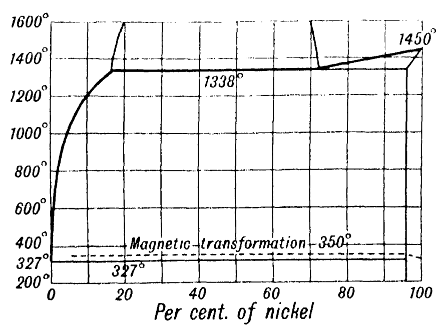


FIG. 149.—The Freezing-point Curve of the Nickel-Lead Alloys.

A. F. Cronstedt,[14] and R. Tupputi prepared **nickel-lead alloys ;** they said that the two metals unite with difficulty to form a grey, slightly lustrous, laminar, and friable alloy. A. D. van Riemsdyk added that if gold be present, the phenomenon of flashing may occur in the cupellation. T. Fleitmann found that up to 10 per cent. of lead may be added to nickel without the alloy losing its working properties. B. S. Summers made lead-nickel alloys electrolytically. J. Cournot studied the properties of the alloys. A. Portevin observed that nickel and lead are only partially miscible in the liquid state, and said that the metals do not form solid soln. Two liquid layers are formed with between 7 and 60 per cent. of nickel at 1365°. The eutectic has 0·07 per cent. of nickel. G. Tammann and W. Oelsen represented the solubility, S per cent., of nickel in lead by $\log S = -2320T^{-1} + 3{\cdot}11$, and found :

	327°	300°	250°	200°	180°
S	0·195	0·103	0·047	0·026	0·023

and, by extrapolation, obtained, at 20°, S=0·000016 per cent. of nickel. W. Seith and co-workers studied the diffusion of nickel in lead. G. Voss found that the alloys are not miscible in the fused state when the proportion of nickel is between 16 and 72 per cent., Fig. 149. There is a series of solid soln. which when saturated contains 4 per cent. of lead. At 1338°, the solid soln. is in equilibrium with the two liquid layers. The solubility of the solid soln. in lead decreases very rapidly

with fall of temp., and at its m.p., lead alone separates out. All the alloys are magnetic; the transition temp. of non-magnetic to magnetic nickel is raised about 5° by the addition of 4 per cent. of lead, and it remains constant at 350° with further additions of lead.

A. M. Fairlie compared lead-nickel alloys against lead-antimony alloys, and found that the lead-nickel alloys have a tensile strength one-third greater than that of lead, but less than half that of the best lead-antimony alloys. The elongation—per cent. per half inch—and the tensile strength in lbs. per sq. in. were:

Lead	100	99	97·75	96·5 per cent.
Elongation	110	74	91	32
Tensile strength	2365	3174	3262	3262

G. Tammann and W. Wiederholt studied the cathodic polarization of the alloy; and J. Cournot, the non-magnetic alloys of the two elements. G. Tammann and W. Oelsen measured the sp. magnetization (gauss) of lead-nickel alloys containing the following proportions of dissolved and total nickel:

		327°	300°	200°	150°	100°	20°
Dissolved Ni		0·195	0·103	0·026	0·023	0·023	0·023
Gauss	0·035 per cent. Ni	−0·200	−0·10	2·86	5·95	5·95	5·95
	0·218 per cent. Ni	10·7	66·6	107·2	112·0	112·1	112·2
	0·520 per cent. Ni	191	229	283	283	282	285

The lead-nickel alloys are in nearly all cases superior to lead in their acid-resisting properties. The lead-nickel alloys can be substituted for lead-antimony alloys where hot acid has to be treated, provided a moderate degree of hardness and strength is all that is desired. The losses in weight with sulphuric acid were:

Per cent. Pb	Sp. gr. 1·530 One week at 14°	Sp. gr. 1·530 One week at 184°	Sp. gr. 1·753 One week at 14°	Sp. gr. 1·753 12 hrs. at 184°
100	0·014	0·357	0·078	0·419
99	0·009	0·190	0·035	0·391
97·75	0·017	0·085	0·042	0·357
96·5	0·021	0·134	0·057	0·199

N. Parravano, W. Guertler and F. Menzel, and G. F. Allen prepared **nickel-lead-copper alloys** and found that the addition of 0·95 to 4·5 per cent. of nickel and 0·05 to 4·5 per cent. of copper renders lead more resistant to attack by water. J. McNeil noted that the presence of 2·5 per cent. of nickel raised the solubility of lead in copper from 35 to 60 per cent. A. Brand found some antimony and sulphur in a complex copper-nickel-lead alloy occurring as a furnace product at Mechernich. W. Guertler and F. Menzel, and W. Guertler found that whilst copper and nickel mix completely in the liquid state and form mixed crystals in the solid state in all proportions, the binary systems copper-lead and nickel-lead show very limited miscibility in the liquid state, the limits for non-miscibility being 36–86·5 per cent. of lead in the first and 30–84 per cent. in the second; nevertheless, the ternary system shows complete miscibility in the liquid state in almost all proportions. Mixtures of the German coinage nickel (Ni 25 per cent., Cu 75 per cent.) with lead in all proportions yielded clean homogeneous alloys of excellent lustre and appearance, the microscopical examination showing mixed crystals of copper-nickel in a ground mass of almost pure lead. Alloys containing 60 per cent. of lead with varying proportions of copper and nickel show complete miscibility in the liquid phase down to very small proportions of either nickel or copper (2·5 per

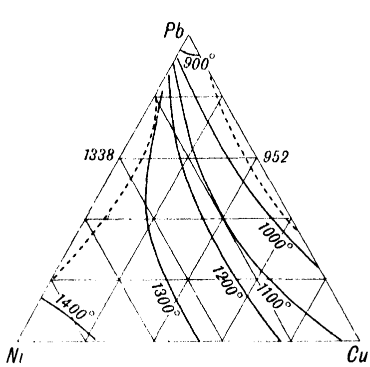


Fig. 150.—The Melting-point Curve of the Nickel-Lead-Copper Alloys.

cent. Ni, 6 per cent. Cu); this is attributed to the fact that a small proportion of either copper or nickel is sufficient to make an otherwise immiscible fluid layer of the other with lead completely miscible. L. Dienelt, and H. von Jüptner prepared some alloys of copper-nickel-lead with zinc and tin. M. Waehlert found that the alloys form a continuous series of solid soln., and are comparatively simple in character. B. Garre and A. Müller studied the **nickel-lead-cadmium alloys**; W. Guertler, **nickel-lead-antimony alloys**; and R. J. Anderson, the **nickel-lead-tin-zinc-copper alloys.**

E. W. von Siemens and J. G. Halske,[15] and K. Grassmann and E. J. Kohlmeyer prepared some **nickel-tantalum alloys** by subjecting an intimate mixture of the powdered metals to a high pressure, and heating the product at a high temp. in an inert atm. or in vacuo. They found that the addition of 5 to 10 per cent. of tantalum to nickel increases materially the acid resistance and the ductility of nickel. An alloy with 30 per cent. of tantalum can be boiled in aqua regia and other acid for an extended period of time without suffering corrosion; it does not oxidize in air at a high temp.; the alloy is very tough; it may be rolled, hammered, and drawn; and it is not brittle. The nickel loses its magnetic properties on adding tantalum.

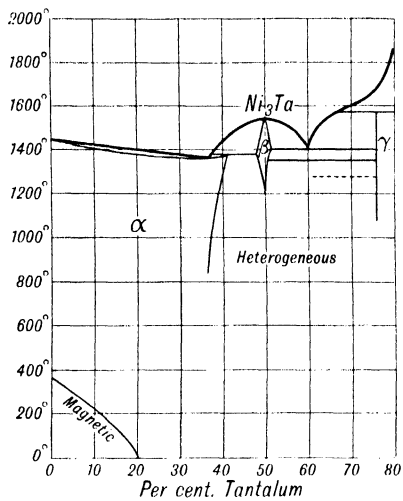


FIG. 151.—The Constitutional Diagram of the Ni-Ta Alloys.

E. Therkelsen discussed these alloys. Alloys with up to 36 per cent. of Ta form a homogeneous solid soln. which has a liquidus falling smoothly from 1450° to 1350°; there is a maximum at 1545°, corresponding with nickel tritatantalide, Ni_3Ta, and a minimum at 1400° with 61 per cent. There are α-, β-, and γ- solid soln.—Fig. 151.

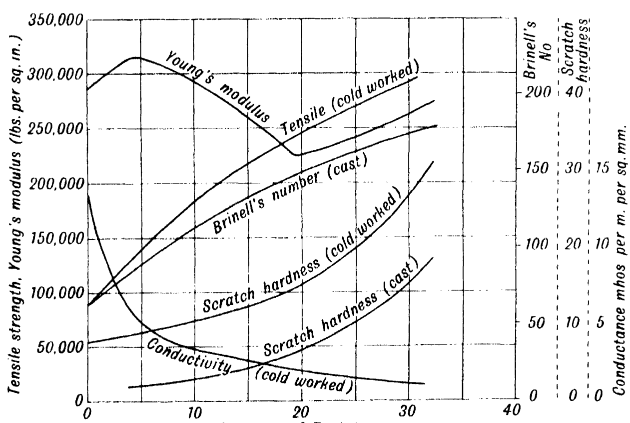


FIG. 152.—Hardness, Tensile Strength, and Electrical Conductivity of the Ni-Ta Alloys.

The structure of alloys with 50 to 78 per cent. of Ta are very complex, and show a transformation in the solid state at 1350°. Brinell's hardness of the solid soln., Fig. 152, increases almost linearly with the tantalum content up to 250 for 35 per cent. of Ta; the tensile strength of the cold-worked alloys increases from 40 tons per sq. in. for pure nickel to 116 tons per sq. in. for the 35 per cent. Ta alloy, Fig. 152. The cold-drawn 9 per cent. Ta alloy has an electrical resistance of

$R=0{\cdot}262(1+0{\cdot}002\theta+0{\cdot}0000016\theta^2)$ ohms per metre per sq. mm.—Fig. 152. The e.m.f. of the couple Ni : 9 to 15 per cent. Ta alloy is 2 m.volt at 100°. The resistance of alloys with about 12·5 at. per cent. of Ta is very good. All the alloys readily oxidize in air at 350°. W. Rohn studied the thermoelectric force of the alloys against platinum; and K. Grassmann and E. J. Kohlmeyer, the **nickel-tantalum-zirconium alloys; nickel-copper-tantalum alloys; nickel-columbium alloys;** and the **nickel columbium-zirconium alloys.**

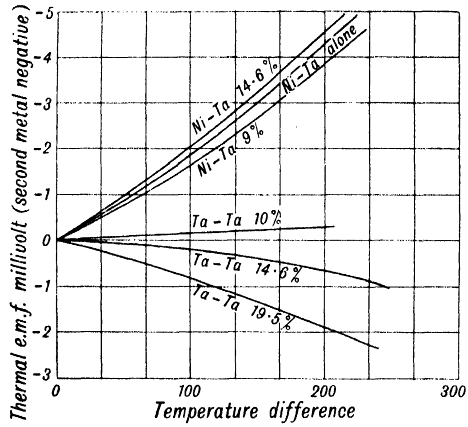


FIG. 153.—The Thermal Electromotive Force of the Ni-Ta Alloys.

H. Giebelhausen,[16] and K. Grassmann and E. J. Kohlmeyer, prepared **nickel-vanadium alloys.** He said that the two elements form a continuous series of solid soln. within the range investigated, *viz.* 0 to 36 per cent. vanadium. The f.p. curve, Fig. 154, passes through a shallow minimum. The magnetic transformation temp. is rapidly lowered by vanadium as shown by the dotted lines—*vide* nickel-vanadium steels. H. Hersenschmidt obtained nickel-vanadium by reducing a mixture of nickel oxide and vanadic acid. W. Rohn studied the thermoelectric force of the alloys against platinum; and K. Grassmann and E. J. Kohlmeyer, the **nickel-copper-vanadium alloys.**

G. Voss[17] prepared **nickel-chromium alloys,** and found that the f.p. curve consists practically of two branches: from 0 to 42 per cent. of nickel, solid soln. rich in chromium separate; and from 42·5 to 100 per cent. nickel, solid soln. rich in nickel separate out. There is a very short break in the miscibility curve between 42·0 and 42·5 per cent. of nickel. Alloys with less than 90 per cent. are more magnetic. The transition temp. is lowered 100° by the addition of 2 per cent. of chromium. S. Sekito and Y. Matsunaga, Y. Matsunaga, and S. Nishigori and M. Hamasumi revised the work of G. Voss, and the results are summarized in Fig. 156. The preparation of the alloys by fusion in hydrogen in magnesia crucibles was executed by C. J. Smithells and co-workers. J. W. Cuthbertson studied the electrodeposition of the alloy. N. B. Pilling and T. E. Kihlgren, P. Röntgen and W. Koch, W. Rosenhain and co-workers, and C. H. M. Jenkins and co-workers, discussed the constitution of the alloys. G. Grube studied the diffusion of chromium in nickel. E. C. Bain, and M. R. Andrews found that the lattices of the chromium and nickel are very different in type, and there is a region extending from about 65 to 95 per cent. chromium where the lattices overlap. F. C. Blake and co-workers observed that with alloys having 65 to 85 per cent. of chromium there is present a phase having a body-centred lattice, which is chromium; there is a phase with chromium nickelide; and a phase with **nickel dichromide,** $NiCr_2$. The X-radiogram indicates that there are 96 atoms per unit cell; that the cell consists of four interpenetrating lattices of nickel, with four other interpenetrating lattices of chromium, the lattice is body-centred and tetragonal, with $a=10{\cdot}64$ A., and an axial ratio $a:c=1:1{\cdot}040$. The density is identical with that of chromium, namely, 6·93. E. R. Jette and co-workers found that the alloys contained only body-centred

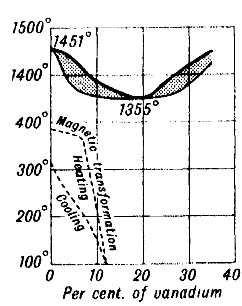


FIG. 154.—The Freezing-point Curve of Nickel-Vanadium Alloys.

chromium, face-centred nickel, and occasionally rhombohedral chromic oxide. F. C. Blake and A. E. Focke discussed the distortion of the nickel space-lattice by chromium. S. Sekito and Y. Matsunaga found that alloys with up to 45 per cent. of chromium have a face-centred, cubic lattice, and the chromium dissolves in the nickel to form a solid soln. Alloys with 95 to 100 per cent. of chromium have a body-centred cubic lattice, and another solid soln. is formed. Alloys with 45 to 95 per cent. of chromium are heterogeneous, and consist of a mixture of the two solid soln. F. Ströhlein investigated the diffusion of chromium in nickel, and Fig. 155 is selected from his results.

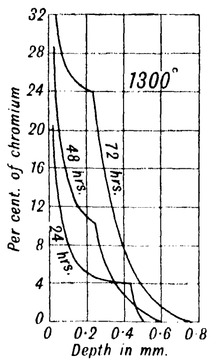


FIG. 155.—The Diffusion of Chromium in Nickel.

A. Parkes prepared a nickel-copper-aluminium alloy with 10 per cent. of chromium; and nickel-chromium alloys were also prepared by H. Ostermann and C. Lacroix, E. Haynes, F. Krupp, M. von Schwarz, J. H. S. Dickenson, F. Hauptmeyer, A. B. Davis, J. H. L. de Bats, W. F. Cochrane, S. A. Pogodin, A. M. Korolkoff, S. A. Pogodin and co-workers, the Vereinigte Deutsche Nikelwerke, W. Hoskins, C. J. Smithells, S. S. Smirnoff, J. H. Russel, Y. S. Gintzburg and A. D. Goldberg, and J. T. H. Dempster. Some of these alloys are employed on account of their large electrical resistance, and their stability at a high temp. for wire-wound electrical furnaces. M. von Schwarz discussed how the wires became brittle with use. The alloy nichrome has roughly 58 to 62 per cent. of Ni; 23 to 26 per cent. of Fe; 8 to 14 per cent. of Cr; 0·5 to 2·0 per cent. of Mn, Zn, and Si; 0·2 to 1·0 per cent. of C. This alloy has the trade name *chromel A;* another grade of nichrome is *chromel B* with 15 per cent. of chromium and 85 of nickel; another grade, *chromel C,* has 11 per cent. of chromium, 64 of nickel, and 25 of iron. Another form of nichrome has Cr, 12; Ni, 60; and Fe, 25; yet another has Cr, 12; Ni, 60; Fe, 26; Mn, 1; C, 0·50; and Si, 0·40.

The X-radiograms of the alloys were studied by Z. Jeffries and R. S. Archer, F. C. Blake, F. C. Blake and J. O. Lord, W. C. Phebus and F. C. Blake, and H. Weiss. J. R. Vilella, and J. A. M. von Liempt studied the solid soln. The sp. gr. of this alloy is 8·15; and the Brinell's hardness, 165 to 175. W. C. Ellis and co-workers gave 8·39 for the sp. gr. of the Ni : Cr(80 : 20) alloy. According to F. Bauerfeld, the action of hydrochloric acid on nickel-chromium alloys represented by the percentage loss is :

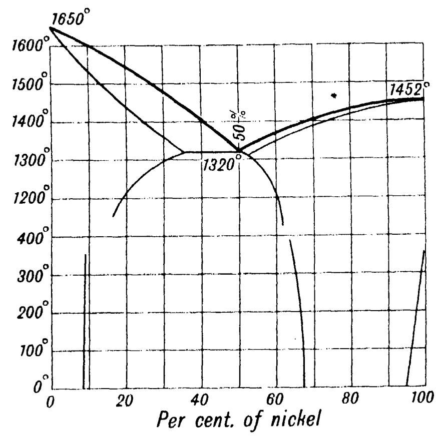


FIG. 156.—Freezing-point Curve of the Nickel-Chromium Alloys.

Ni	89·90	86·01	—	65·29	44·57	—
Cr	—	2·38	10·59	22·14	43·20	100
C	5·12	6·28	4·95	5·28	5·00	—
Loss	0·36905	0·47231	0·25081	0·07422	0·1490	4·00156
E 50°	1·2	2·5	2·3	2·3	2·1	—
E 200°	3·7	9·3	6·9	6·2	5·9	—
E 400°	9·6	20·8	23·0	18·8	17·8	—
E 600°	17·1	32·9	33·3	30·8	29·3	—
E 800°	24·4	45·3	45·9	44·1	41·6	—

A. G. Lobley and C. L. Betts, and C. R. Austin and G. R. Gier, measured the creep of the 80 : 20 nickel-chromium alloy. C. J. Smithells and S. V. Williams found the diffusion of nickel and chromium at 1450° is very small.

P. W. Bridgman found the compressibility of nichrome (Ni, 80; Cr, 20) at 30° to be $\delta v/v_0=(5\cdot50-0\cdot0_415p)p\times10^{-7}$, or $\beta=0\cdot0_655$ at 30°, and R. F. Mehl and B. J. Mair obtained a higher value by calculation from the mixture rule. The mechanical properties were examined by W. Rosenhain and co-workers, C. H. M. Jenkins and co-workers, P. Chévenard, J. F. Kayser, H. J. Tapsell and J. Bradley, R. S. MacPherran, N. L. Mochel, E. F. Lake, J. K. Smith, M. Combe, W. Rohn, F. A. Fahrenwald, A. le Chatelier, L. O. Hart, F. Jablonsky, and B. Jones. The ultimate tensile strength of nichrome is:

	200°	400°	600°	800°
Tensile strength	94,000	91,000	59,000	32,000 lbs. per sq. in.

P. Chévenard, and F. A. Fahrenwald measured the thermal expansion of the alloys, the sp. ht., the thermal conductivity, and the radiation of heat. P. Chévenard observed an *anomalie*—that is, a break, *A*, Fig. 157—in the continuity of the coeff. of thermal expansion curve of the chromium-nickel alloys. The results are summarized in Fig. 157. Observations were also made by P. Hidnert. The

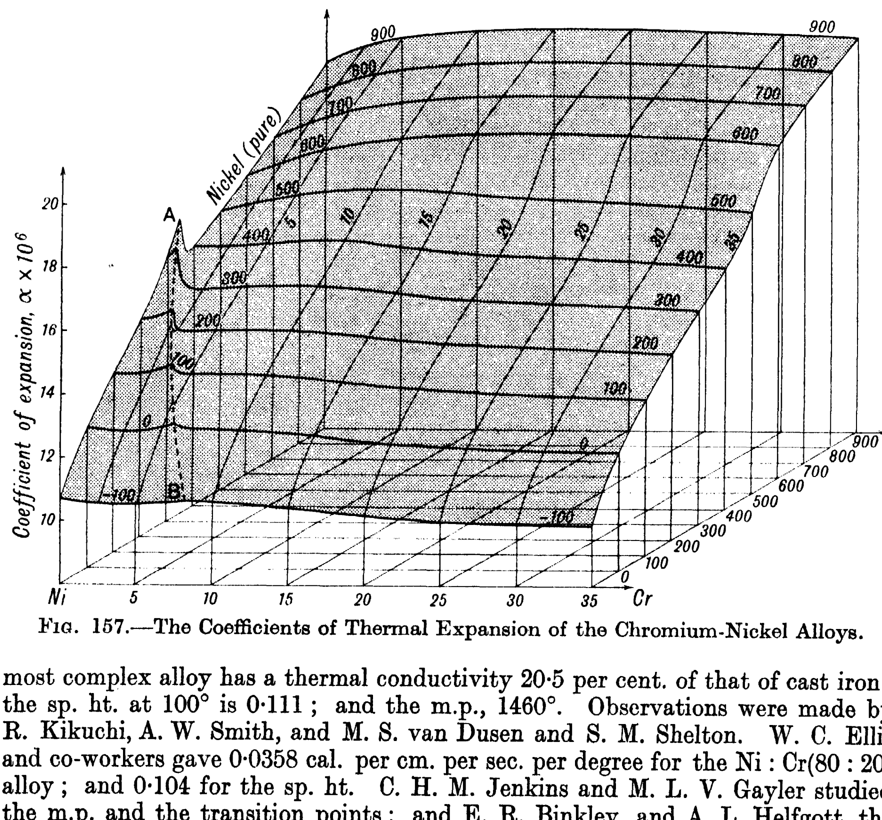


FIG. 157.—The Coefficients of Thermal Expansion of the Chromium-Nickel Alloys.

most complex alloy has a thermal conductivity 20·5 per cent. of that of cast iron; the sp. ht. at 100° is 0·111; and the m.p., 1460°. Observations were made by R. Kikuchi, A. W. Smith, and M. S. van Dusen and S. M. Shelton. W. C. Ellis and co-workers gave 0·0358 cal. per cm. per sec. per degree for the Ni : Cr(80 : 20) alloy; and 0·104 for the sp. ht. C. H. M. Jenkins and M. L. V. Gayler studied the m.p. and the transition points; and E. R. Binkley, and A. L. Helfgott, the emissivity. V. A. Suydam found the total radiation energy of nichrome, *E* watts per sq. cm., at *T*° K., to be—*vide* Fig. 24:

	325°	483°	673°	1013°	1113°	1178°	1258°	1308° K.
E .	0·0417	0·3259	0·9080	1·8913	3·6580	5·9170	9·8000	13·3820

A. W. Foster gave for the at. ht. of nickel:

	397°	347°	342°	331°	269°	144°
At. ht.	8·22	8·10	9·26	10·13	7·70	6·88

for an alloy with 1 per cent. of chromium :

	341°	302°	283°	235°	195°	107°
At. ht.	7·03	7·29	8·11	6·98	6·50	6·15

and for an alloy with 2 per cent. of chromium :

	354°	309°	244°	229°	183°	127°
At. ht.	6·34	5·99	6·12	5·90	5·65	5·40

F. M. Sebast and G. L. Gray found the electrical resistance R microhms per cm. cube at 20°, of the Ni : Cr alloys for 100 : 20 to be R and the temp. coeff. α=0·00012 ; for 100 : 15, R=84·7 and α=0·00020 ; 100 : 10, R=67·8 and α=0·00037 ; and for 100 : 5, R=45·7 and α=0·00097. W. C. Ellis and co-workers gave for the electrical conductivity of the Ni : Cr(80 : 20) alloy, $k\times10^{-5}$=0·0939 mho. Measurements were made by W. A. Gatward, M. A. Hunter and A. Jones, F. V. Lindsay, M. A. Grossman, J. Strauss, and R. Kikuchi. H. Rolnick studied the tension coeff. of the resistance of nichrome.

V. A. Suydam gave for the resistance of nichrome R ohms at different temp., °K, when the resistance at 0° or 273° is taken as unity :

	273°	398°	556°	735°	1018°	1188°	1320°	1503°
R	1·000	1·045	1·088	1·128	1·143	1·169	1·219	1·279

A. A. Somerville's results are summarized in Fig. 158. P. W. Bridgman gave for the press. coeff. of the resistance for press. between 0 and 12,000 kgrms. per sq. cm. ; chromel A, $-0{\cdot}0_6134$ at 0°, and $-0{\cdot}0_6137$ at 90°, whilst the temp. coeff. between 0° and 100° is 0·000163. Similarly, for chromel B, the press. coeff. at 0° was $-0{\cdot}0_6158$, and at 95° $-0{\cdot}0_6169$, whilst the temp. coeff. between 0° and 95° was 0·000212. For chromel C, the press. coeff. at 0° was $-0{\cdot}0_64272$; at 52·24°, $-0{\cdot}0_64194$; and at 95·88°, $-0{\cdot}0_64488$ for press. between 0 and 12,000 kgrms., and $-0{\cdot}0_64372$ for press. between 0 and 6000 kgrms. so that between 0° and 100° the press. coeff. passes through a minimum. The temp. coeff. at atm. press. is normal in being positive, but the direction of the curvature is not normal. Between 0° and 52°, the temp. coeff. is 0·001076, and between 0° and 96°, 0·001030. H. Rolnick measured the effect of tension on the resistance of nichrome ; H. L. Brakel, the effect of vibration ; and J. Obata, the effect of a magnetic field. W. R. Barclay and G. E. M. Stone found the Ni : Cr=80 : 20 curves to be useful for heating electric furnaces up to 1100°. F. P. Peters, M. A. Hunter and A. Jones, and S. F. Schemtschuschny and co-workers, made observations on the subject. A. Imhof observed stationary waves are emitted by wires heated by an alternating current. C. G. Fink and C. M. Decroly found the contact potential of nichrome (60·8 Ni, 12·5 Cr, 26·3 Fe) in sulphuric acid of 0·45, 2·40, 5·15, and 9·92 per cent. H_2SO_4 to be—0·610, —0·725,—0·717, and —0·710 volt. They also studied the passivity of the alloy.

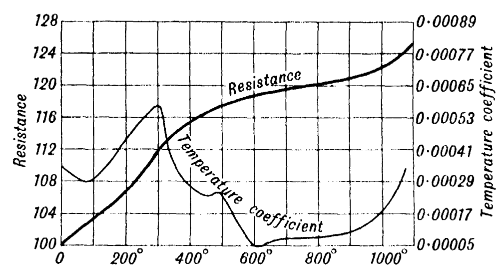


FIG. 158.—The Effect of Temperature on the Resistance of Nichrome.

For O. L. Kowalke's observations on the thermoelectric force of couples of cobalt with nichrome and the "advance" alloy, *vide supra*, cobalt ; E. F. Northrup, and R. Hase measured the e.m.f. of a thermocouple of nickel and nichrome. The thermoelectric force, E millivolts, of some nickel-chromium alloys, measured by F. Bauerfeld, are indicated above ; that of the alloys against platinum was studied by W. Rohn, and L. J. Neuman ; and against copper, by A. W. Foster. O. L. Kowalke obtained the results summarized in Fig. 159 for the couples (i) Ni, 86 ; Cr, 14·3, and Ni, 96·6 ; Fe, 2·2 ; Si, 2·4 ; (ii) Cr, 10·01 ; Fe, 30 ; Ni,

59·9, and Al, 3·3; Ni, 96·4; (iii) Fe, 99·9, and Al, 1·14; Ni, 98·3; (iv) nickel with a small proportion of iron, and iron with a small proportion of nickel; (v) Fe, 99·8, and Cu, 52·3; Ni, 48·0; (vi) Cr, 16·8; Ni, 83·3, and Fe, 1·08; Ni, 98·90. The results for (vi) were similar to those with (ii); the values for the thermoelectric force, E millivolts, of the other couples were:

	324°	454°	554°	646°	825°	1018°	1115°
E (i) . . .	11·39	16·64	20·73	24·41	31·51	38·45	41·43
	316°	450°	545°	636°	800°	824°	993°
E (ii) . . .	5·56	8·59	10·76	13·10	18·27	22·21	24·52
	240°	330°	435°	645°	843°	1026°	1109°
E (iii) . . .	6·75	9·09	10·66	13·64	18·20	22·19	24·16
	360°	452°	643°	836°	931°	1022°	1107°
E (iv) . . .	8·41	10·40	14·98	20·65	23·60	26·57	29·58
	318°	445°	540°	634°	825°	896°	997°
E (v) . . .	15·70	22·51	27·66	32·99	44·85	49·41	55·02

A. W. Foster, and W. Rohn studied the thermoelectric force of the alloys; and A. W. Smith, the Hall effect. A. W. Foster, and M. A. Hunter and A. Jones measured the thermoelectric force of alloys of chromium and nickel against copper, and the results are indicated in Fig. 49 in connection with nickel. O. Feussner discussed the subject. J. Safranek investigated the magnetic properties of the nickel-chromium alloys, and found that the reciprocal of the susceptibility plotted against temp. gives a straight line becoming concave towards the T-axis at higher temp. The various magnetic constants are linear functions of the composition. The sp. magnetization of the $CrNi_6$ alloy extrapolates to zero at absolute zero. C. Sadron observed that the Curie point of nickel falls from 355° with nickel to −143° with nickel containing 10 per cent. of chromium, and to −273° (extrapolation) when 12 per cent. of chromium is present. The saturation magnetization of the alloys, σ_T, at T° K., in a particular field, varies with the temp. between 110° K. and 150° K., so that $\sigma_T=\sigma_0(1-aT)$, when a is constant. P. Chévenard, and D. P. Ray-Chaudhury and P. N. Sen Gupta studied the magnetic properties of the alloys, and J. M. Ide, the magnetostriction.

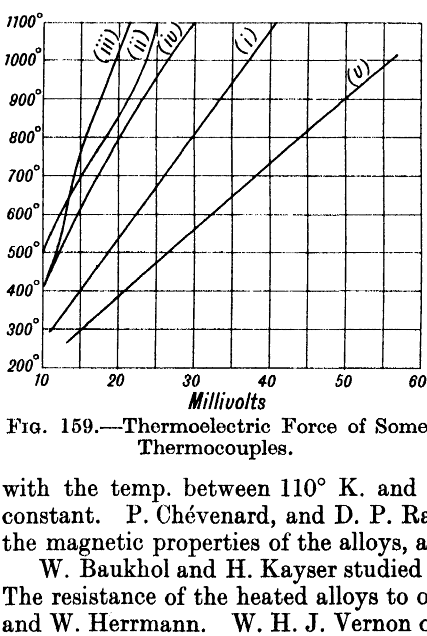


FIG. 159.—Thermoelectric Force of Some Thermocouples.

W. Baukhol and H. Kayser studied the permeability of the alloys to hydrogen. The resistance of the heated alloys to oxidation was studied by F. A. Fahrenwald, and W. Herrmann. W. H. J. Vernon observed that chromium hinders the fogging of nickel on exposure to air—*vide* nickel; Y. Utida and M. Saito, that nichrome wire on a 2 hrs.' heating gained 0·84 mgrm. of oxygen per sq. cm. They also examined the effect with other resistance wires. R. J. McKay, J. C. Hudson, and J. A. N. Friend discussed the corrosion of the alloy by sea-water, etc. H. Ipavic studied the corrosion of the alloy by hydrogen sulphide. R. Coustal and H. Spindler found that anodes of nickel-chromium are slightly attacked by liquid ammonia. Y. Utida and M. Saito studied the resistance to corrosion of nichrome by sulphuric acid at 20° using 125 c.c. of acid for a sample of 10 grms. for 333 hrs., and for 24 hrs. at 80° and 47 hrs. at 20°. The losses in grams per sq. in. per hour were:

	20°					80°		
Sp. gr. H_2SO_4 .	1·830	1·747	1·408	1·142	1·036	1·830	1·408	1·036
Loss . .	0·00007	0·00019	0·000	0·000	0·00006	0·004	0·0010	0·0004

The corrosion with nitric acid is rather severe; and with hydrochloric acid, the action is not severe with up to 20 per cent. acid in the cold. The action with sulphurous acid is six times that of sulphuric acid of sp. gr. 1·830 under similar conditions. The action of acetic acid is severe. The alloy is very little attacked by lactic acid, or by aq. ammonia of any concentration. P. Askenasy noted the resistance of nickel-chromium to steam at 1000°; H. Gruber, the resistance to hydrogen sulphide; and J. S. Vanick, the resistance to hot gaseous ammonia. W. Rohn found the corrodibility of nickel : chromium alloys holding 1 per cent. of manganese, and expressed as a loss in grams per sq. dm., N not annealed, A, annealed, using 10 per cent. acids:

		HNO_3		H_2SO_4		HCl		CH_3COOH		H_3PO_4	
		N	A	N	A	N	A	N	A	N	A
88 : 11	24 hrs. cold	2·76	2·37	0·03	0·02	0·18	0·10	0·002	0·002	0·004	0·004
	1 hr. hot.	2·16	0·9	0·12	0·05	1·26	1·10	0·007	0·007	0·018	0·03
84 : 15	24 hrs. cold	0·04	0·04	0·07	0·01	0·08	0·04	0·006	0·004	0·006	0
	1 hr. hot	0	0·2	0·10	0·02	1·20	0·51	0·004	0·004	0·034	0·032
79 : 20	24 hrs. cold	0·01	0·02	0·01	0·01	0·03	0·03	0·002	0·002	0·002	0·004
	1 hr. hot	0	0	0·11	0·14	0·72	0·68	0	0	0·011	0·051

Observations were made by W. Guertler and W. Ackermann, R. Borchers, W. R. Barclay, P. Chévenard, W. A. Gatward, L. O. Hart, J. F. Kayser, F. F. Khimushin and M. F. Denisoff, P. S. Menough, W. M. Mitchell, M. Sauvageot, S. W. G. Snook, B. Strauss, F. Ströhlein, and W. H. J. Vernon. C. G. Fink and C. M. Decroly found that the losses with nichrome (60·8 Ni, 12·5 Cr, 26·3 Fe), in milligrams per sq. dm. per 24 hrs., were, with sulphuric acid having the concentration, in grams per litre:

H_2SO_4	3·35	24·75	53·00	106·50	197·90	1570	1768
Loss	69	123	173	231	315	145	700

W. G. Imhoff studied the corrosive action of molten zinc on the nickel-chromium alloys; G. Nordström, the attack by hydrogen sulphide, sulphur dioxide, and reducing gases; H. McK. Elsey, carbonizing the alloy by heating it in nitrogen and a hydrocarbon. E. Maass and W. Weiderholt found the attack by dry salts decreases in this order: magnesium chloride, carnallite, Hartsalz, potassium chloride, sodium chloride, and magnesium sulphate. E. Siedschlag found that the copper-chromium-nickel alloy (5 : 40 : 55), and 150 c.c. of liquid acting for 1 hr. gave the following percentage losses: Hot, conc. aqua regia, 29·0; cold, conc. aqua regia, 22·0; hot, hydrochloric acid (1 : 1), 5; hot, conc. hydrochloric acid, 18; cold, conc. hydrochloric acid, 1·2; hot, conc. nitric acid, 0·4; cold, conc. nitric acid, 0·3; hot nitric acid (1 : 1), 0·1; hot sulphuric acid (1 : 1), 0·1; and soda-lye, nil. With the 30 : 10 : 60 alloy, hot, conc. aqua regia, 28·0; cold, conc. aqua regia, 3·0; hot conc. hydrochloric acid, 8·0; hot hydrochloric acid (1 : 1), 16·0; hot sulphuric acid, 0·7; hot, conc. nitric acid, 0·1; cold, conc. nitric acid, 0·1; and soda-lye, nil. R. Borchers studied the action of nitric acid; and C. G. Fink and F. J. Kenny, the passivity of the alloy produced by chromic acid. E. C. Badeau, and W. A. Wesley and co-workers noted the action of hot, aerated milk on the alloy. R. Hase studied the resistance of nichrome to molten brass, and zinc; and F. H. Rhodes and co-workers, to phenols. The corrodibility of the alloys was discussed by J. Strauss.

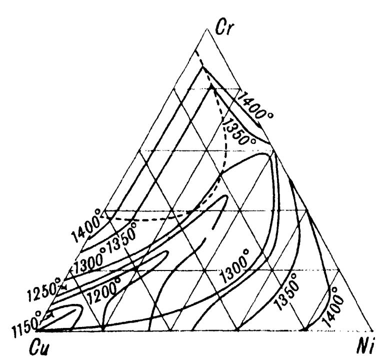


Fig. 160.—Isothermal Curves of the Copper-Chromium-Nickel Alloys.

E. Siedschlag studied the ternary copper-chromium-nickel alloys and obtained the isothermal curves indicated in Fig. 160. The heterogeneity of the copper-

chromium system is partly removed by the addition of nickel; when below 55 per cent. of nickel is present, heterogeneous systems with two layers are formed in the region within the dotted line, Fig. 160. D. F. McFarland and O. E. Harder measured the sp. gr., Brinell's hardness, and the modulus of elasticity and the ultimate tensile strength in lbs. per sq. in. of some ternary copper-nickel-chromium alloys, and the results are summarized in Table IX. The elongations were small.

TABLE IX.—MECHANICAL PROPERTIES OF COPPER-NICKEL-CHROMIUM ALLOYS.

Composition		Hardness (Brinell's)	Sp. gr.	Modulus elasticity (lbs. per sq. in.)	Ultimate strength (lbs. per sq. in.)
Cu	Cr				
91·68	9·32	<68	8·78	—	—
82·13	8·40	86	8·57	—	—
74·43	8·45	103	8·81	18,000,000	19,978
62·58	8·53	143	8·72	—	—
52·57	8·69	161	8·75	—	—
42·40	8·67	163	8·62	—	23,833
83·02	16·98	69	8·60	—	—
73·22	17·12	82	8·71	7,000,000	14,880
63·28	17·25	89	(8·34)	12,000,000	14,802
53·16	17·40	99	8·62	20,000,000	17,521
42·88	17·54	156	8·52	—	—
32·41	17·69	175	8·54	—	56,255
21·80	17·83	179	8·50	7,000,000	19,846
10·99	17·98	126	8·48	—	—
74·05	25·95	68	8·47	—	—
63·99	26·17	117	8·55	—	—
53·77	26·38	116	8·49	17,600,000	22,650
43·47	26·61	126	8·42	20,000,000	25,768
32·79	26·84	148	8·34	16,300,000	38,734
22·05	27·06	170	8·34	23,700,000	32,654
11·12	27·29	163	8·36	22,000,000	29,630
—	27·52	181	8·23	15,000,000	36,958
54·38	35·58	121	8·33	—	—
43·86	35·89	116	8·38	—	—
33·17	36·20	131	8·14	26,400,000	7,449
22·31	36·50	156	8·12	—	—
11·25	36·82	163	8·13	16,300,000	29,587
—	37·14	147	8·14	—	—
33·57	45·76	107	8·24	57,000,000	33,842
22·58	46·16	—	—	63,200,000	22,336
11·39	46·56	202	7·87	—	—
—	46·96	179	7·95	48,000,000	37,200
11·53	56·56	228	—	—	—
—	57·07	179	—	—	—

Observations were also made on the microstructure and working qualities of these alloys. G. Klein studied these alloys. F. M. Sebast and G. L. Gray investigated the electrical resistance of the copper-nickel-chromium alloys. They found for the resistance R microhms per cm. cube at 20°, and for the temp. coeff. α, on adding the following proportions of chromium to 100 parts of the copper-nickel alloy,

25 Cr	Nickel .	90	84	80 per cent.			
	R .	107	110·8	121·8			
20 Cr	Nickel .	100	90	75	50	25	0 per cent.
	R .	96·4	106·3	86·3	36·7	21·3	2·7
	α .	0·00012	0·000079	0·00012	0·00031	0·00046	0·00299
15 Cr	Nickel .	100	90	85	75	25	0 per cent.
	R .	84·1	95·7	99·0	86·4	22·1	3·4
	α .	0·00020	—	—	0·00011	0·00047	0·0025

10 Cr	Nickel .	100	85	75	50	25	0 per cent.
	R . .	67·8	86·3	83·9	50·7	22·4	2·2
	a . .	0·00037	—	0·00016	0·00018	0·00042	0·00349

5 Cr	Nickel .	100	75	50	25	0 per cent.
	R . .	45·7	70·5	55·1	25·1	2·1
	a . .	0·00097	0·00041	0·00014	0·00035	0·00345

The results are plotted in Fig. 161. On adding chromium to a copper-nickel alloy, the resistance first rises, and then falls. A maximum resistance is attained for each alloy at a certain concentration of chromium, and as the concentration of the copper in the alloy increases, this maximum approaches the axis of zero chromium. In all cases where the resistance of an alloy is increased by chromium, the temp. coeff. is reduced; and where the resistance is reduced by adding chromium, the temp. coeff. is increased. E. Siedschlag studied the **chromium-nickel-copper alloys**; J. G. Thompson and co-workers, and A. L. Norbury and E. Morgan, the action on **nickel-chromium-silicon alloys** of soln. of urea and of ammonium carbonate, and likewise also with **nickel-chromium-vanadium alloys**; R. Nitzsche, the acid-resisting properties of the **nickel-chromium-copper-tin alloys**; V. O. Homerberg and I. N. Zavarine, and P. Röntgen and W. Koch, **nickel-chromium-aluminium alloys**; and P. Röntgen and W. Koch, **copper-nickel-chromium-aluminium alloys.** Alloys with the following percentage proportions of nickel and chromium together with about 3 per cent. of iron, and varying proportions of carbon and silicon, were found by F. Bauerfeld to have the following values for the thermoelectric force in millivolts against platinum:

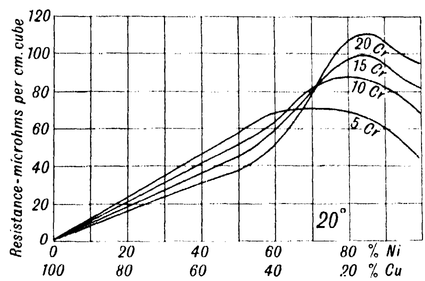


FIG. 161.—The Electrical Resistance of the Cu-Ni-Cr Alloys.

Ni : Cr	50°	100°	200°	300°	400°	500°	600°	700°	800°
89·90 . .	1·2	2·1	3·7	6·9	9·6	13·3	17·1	20·8	24·4
72·63 : 8·06 .	2·3	4·5	10·1	16·1	22·7	29·5	36·2	43·2	—
62·56 : 27·97 .	2·0	3·6	7·7	12·2	17·3	22·7	29·8	36·2	42·4
50·96 : 38·67 .	1·7	3·5	7·0	11·1	15·6	20·0	25·2	31·0	36·6
44·57 : 43·20 .	2·1	4·1	7·9	12·5	17·8	23·5	29·3	35·3	41·6

The alloy Cu : Ni : Cr, 12·5 : 70·8 : 16·7, has a high resistance, *viz.* 112 microhms per cm. cube, and a very small temp. coeff., *viz.* 0·000078. S. W. Parr obtained an alloy, Cu, 6·42; Mn, 0·98; Si, 1·04; W, 2·13; Ni, 60·65; Al, 1·09; Fe, 0·76; Cr, 21·07; and Mo, 4·67, which he called *illium.* The tensile strength is high, it resists corrosion by acids; it is close-grained; and it melts at 1600°. It was used in place of platinum for calorimeter bombs. The alloy *chromax* has Cr, 3; Ni, 14; Cu, 66; Mo, 3; Al, 3; Zn, 12; and *calorite*, Cr, 12; Fe, 15; Mn, 8; Ni, 65. The alloy with the trade-name *chroman* contains up to 20 per cent. Fe; 63 to 88, Ni; 15, Cr; 1, Ni; and the alloy *contracid*, 12 to 20, Fe; 58 to 61, Ni; 15, Cr; 2, Mn.

F. E. Bash's observations of the thermoelectric force of the Ni-Cr-Cu alloys against platinum are indicated in Fig. 48, in connection with nickel. A. Kussmann and B. Scharnoff observed no relation between the coercive force and hardness.

D. F. McFarland and O. E. Harder obtained for the corrosion of the ternary alloys the results indicated in Table X, using normal nitric, hydrochloric, and sulphuric acids; normal soln. of sodium chloride, and hydroxide; ammonium hydroxide, and fatty acids. The results are expressed in terms of the loss of weight in mgrms. per sq. in. per week. H. A. Trebler and co-workers studied the action of milk.

N. Baar[18] prepared **nickel-molybdenum alloys** by fusing the metals in hydrogen in crucibles lined with magnesia. The f.p. curve of alloys with up to 60 per cent. of molybdenum shows the presence of only one compound, nickel molybdide, NiMo; and it melts with decomposition at 1340°. There is a

TABLE X.—THE CORROSION OF THE COPPER-NICKEL-CHROMIUM ALLOYS.

Composition		NaCl	HCl	H_2SO_4	HNO_3	NaOH	NH_4OH	Fatty acids
Cu	Cr							
72·43	8·45	1·89	6·3	11·90	10·80	0·26	33·70	7·70
62·58	8·53	1·53	4·8	14·00	9·90	0·10	34·40	—
52·57	8·60	0·66	6·0	5·10	8·50	0·00	14·30	—
42·40	8·67	0·53	4·6	6·70	10·80	0·00	0·23	0·00
32·05	8·75	0·71	8·2	5·30	15·10	2·60	3·60	—
21·55	8·81	0·63	7·3	12·30	17·20	2·70	0·97	1·14
10·87	8·89	0·60	10·7	4·90	17·80	0·00	0·76	—
—	8·96	0·00	19·4	6·00	980·00	2·70	2·65	—
83·02	16·98	4·00	38·3	14·20	13·10	9·70	57·80	—
73·22	17·12	3·65	29·5	14·50	16·30	5·00	47·70	6·40
63·28	17·25	0·76	33·3	9·00	13·40	0·00	29·50	—
53·16	17·40	2·13	8·2	4·10	10·50	1·20	26·60	6·60
42·88	17·54	0·94	6·2	3·70	7·60	0·14	23·70	3·80
32·41	17·69	0·85	18·8	9·40	6·20	0·00	21·20	0·87
21·80	17·83	0·37	4·4	4·10	17·70	0·00	0·26	—
10·99	17·98	0·51	6·1	7·40	18·10	0·00	0·00	0·25
74·05	25·95	4·60	30·3	16·40	60·30	0·86	67·50	10·70
63·99	26·17	3·30	10·8	15·60	10·84	6·90	49·20	—
53·77	26·38	2·62	5·0	6·10	7·50	0·64	28·30	7·50
43·37	26·61	1·37	6·6	5·30	4·80	0·58	39·60	—
32·79	26·84	1·05	12·3	9·60	4·80	0·09	35·60	3·80
22·05	27·06	0·37	11·6	5·10	4·90	0·00	29·50	—
11·12	27·39	—	5·9	1·80	4·90	0·30	0·00	—
—	27·52	0·37	8·10	4·10	492·00	0·00	0·00	8·30
54·38	35·58	2·95	15·2	14·90	9·20	3·90	50·80	11·30
43·86	35·89	1·84	7·5	12·40	8·30	1·10	41·40	—
33·17	36·20	1·67	11·5	11·00	7·30	1·00	37·50	2·90
22·31	36·50	1·25	18·6	8·00	4·40	0·15	31·50	—
11·25	36·82	0·45	10·0	1·30	1·02	0·22	0·90	0·34
—	37·14	0·40	21·2	2·20	0·60	0·53	0·00	—
33·57	45·76	2·45	16·2	13·20	9·70	5·70	44·80	3·25
22·58	46·16	0·87	9·5	5·60	6·40	0·25	25·30	—
11·39	46·56	0·37	19·5	6·40	7·40	1·00	0·90	2·40
—	46·96	0·27	31·2	0·35	0·00	0·14	0·00	—
11·53	56·56	0·33	11·9	3·70	7·70	1·00	0·20	—
—	57·07	0·27	32·2	1·30	0·35	0·44	0·50	—

eutectic at 1297° or 1300° with 49·5 per cent. of molybdenum. The nickel can hold up to 33 per cent. of molybdenum in solid soln. The subject was studied by P. Röntgen and W. Koch. R. Schwarz studied the diffusion of molybdenum in nickel, and a selection of his results is shown in Fig. 163. V. Adelsköld and co-workers observed no evidence of the formation of complex carbides in the system Ni–Mo–C. W. Köster, and W. Köster and W. Schmidt studied the lattice parameters; W. Rohn, the thermoelectric force of the alloys against platinum; W. Meissner and co-workers, the resistance at very low temp.; W. Köster and W. Schmidt, the magnetic properties of the alloys; J. Cournot, the non-magnetic alloys of the two elements; L. F. Dreibholz, the hardness; W. Guertler, some mechanical properties; and L. F. Dreibholz, and C. Sadron, the magnetic properties. W. Guertler and T. Liepus observed that alloys of nickel and 1 to 30 per cent. molybdenum are in general stable for less than 8 hrs. in contact with 10 and 50 per cent. nitric acid, hot or cold; carbon dioxide and air; citric and tartaric acid, and 50 per cent. aq. ammonia, but they are stable for 48 hrs. in 10 per cent. aq. ammonia. The alloys are stable for 48 hrs. in 10 per cent. sulphuric acid, and 8 hrs. in 20 per cent. sulphuric acid sat. with sodium sulphate, and also in acetic acid; it is stable for 8 hrs. in 50 per cent. sodium sulphide, and for 48 hrs. in a 10 per cent. soln. The alloy is stable for 48 hrs. in 10 and 50 per cent.

soda-lye, and in hydrogen dioxide in a soln. of soda-lye, and in a soln. of sodium sulphide (4 per cent.) and alkali (8 per cent.). It slowly decomposes a soln. of mercuric chloride. It is stable 24 hrs. in a soln. of chlorine water, sea-water, and rain-water, and a soln. of magnesium chloride. The effects of additions of 4 to 10 per cent. of aluminium, of 4 to 13 per cent. of tin, and 1 to 10 per cent. of silicon were also examined. H. O. Forrest and co-workers, and B. E. Field examined the resistance of these alloys by acids, etc. E. Keunecke discussed

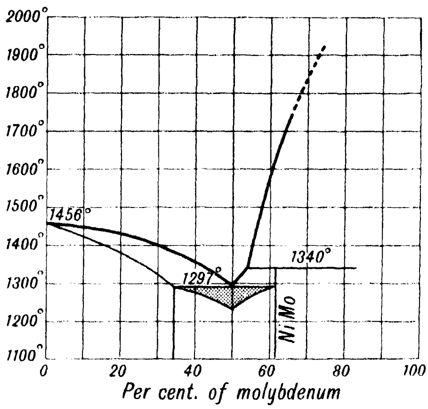


FIG. 162.—The Freezing-point Curves of Nickel-Molybdenum Alloys.

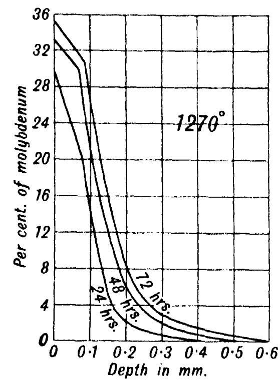


FIG. 163.—The Diffusion of Molybdenum in Nickel.

nickel-molybdenum as a catalyst in the synthesis of ammonia. K. Grassmann and E. J. Kohlmeyer studied the alloys.

W. Guertler and T. Liepus, and K. Grassmann and E. J. Kohlmeyer, examined the **nickel-copper-molybdenum alloys,** and the **nickel-copper-molybdenum-tantalum alloys;** H. Pfautsch, F. Siedschlag, and P. Röntgen and W. Koch studied the **molybdenum-nickel-aluminium alloys;** and H. Pfautsch showed that in the **molybdenum-nickel-silicon alloys,** besides the binary compounds $MoSi_3$, MoNi, Ni_2S, Ni_3S_2, and NiSi, there are two ternary compounds: **nickel**

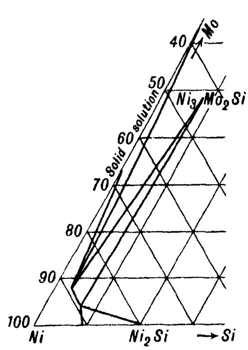


FIG. 164.—Nickel-Molybdenum-Silicon Alloys.

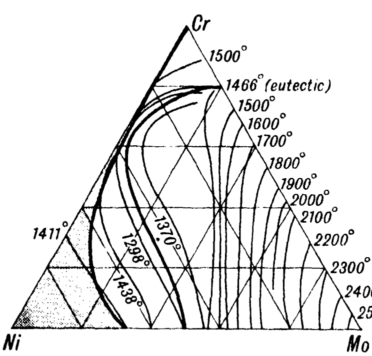


FIG. 165.—Nickel-Molybdenum-Chromium Alloys.

dimolybdenosilicide, Ni_3Mo_2Si, Fig. 164, which is stable below 2100° when it melts unchanged, but the second compound: **nickel molybdenodisilicide,** Ni_4MoSi_2, decomposes below 850°, $2Ni_4MoSi_2 = Ni_3Mo_2Si + Ni_3Si_2 + Ni_2Si$. The silicide NiSi forms a eutectic with Ni_3Mo_2Si. All the alloys, excepting those rich in nickel and consisting of homogeneous solid soln., are hard and brittle. The alloys with over 70 per cent. nickel were all attacked by a soln. of magnesium chloride; the alloy Ni : Mo : Si = 90 : 7 : 3 was not attacked by 48 hrs.' exposure

to 16 per cent. hydrochloric acid, but the others were attacked; they were all attacked by nitric acid; and only the 94 : 3 : 3 alloy was not attacked by tartaric acid. Some of the alloys were attacked and others were not attacked by soln. of sodium hydroxide, sodium sulphide, aq. ammonia, and mixtures of sodium sulphate and sulphuric acid. W. Guertler and T. Liepus studied the corrodibility of these alloys. H. Pfautsch studied the **molybdenum-nickel-tin alloys.** T. D. Kelly, C. J. Smithells and co-workers, G. L. Sakharoff and co-workers, and E. Siedschlag examined the **molybdenum-nickel-chromium alloys,** and found that no ternary compounds are formed, but there is evidence of the formation of a ternary alloy with between 5 and 10 per cent. of nickel. The structure of the alloys rich in nickel is that of a homogeneous solid soln., but the other alloys contain two or three phases consisting of MoNi, molybdenum with small quantities of nickel and chromium in solid soln., and the homogeneous solid soln. The alloy with Ni : Mo : Cr = 60 : 20 : 20 is attacked only slightly by hot hydrochloric acid, or by hot dil. sulphuric acid, and it is not attacked by alkali-lye. H. Gruber studied the action of hydrogen sulphide between 700° and 1000°. W. Guertler and T. Liepus studied the corrodibility of these alloys. E. R. Johnson and W. J. Buechling, and M. Combe studied the **chromium-molybdenum-nickel alloys;** and K. Grassmann and E. J. Kohlmeyer, the **molybdenum-tantalum-nickel alloys;** and the **molybdenum-vanadium-nickel alloys.**

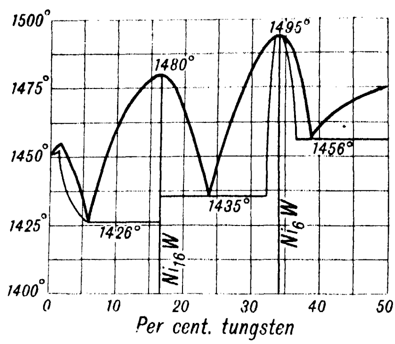


FIG. 166.—The Freezing-point Curve of Nickel-Tungsten Alloys.

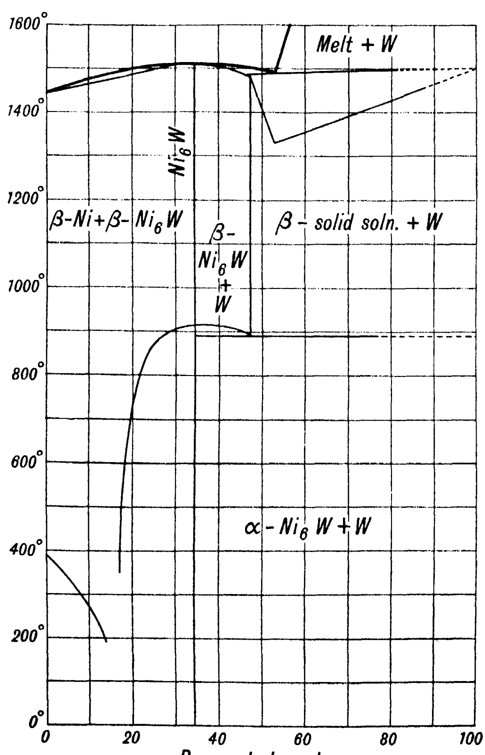


FIG. 167.—Equilibrium Diagram of the Nickel-Tungsten Alloys.

F. A. Bernoulli,[19] J. Trowbridge and S. Sheldon, C. L. Sargent, V. I. Tretyakoff and N. D. Titoff, H. L. Coles and J. G. Donaldson, K. Grassmann and E. J. Kohlmeyer, and H. Leiser prepared **nickel-tungsten alloys;** but H. List said that true alloys are not formed. R. Irmann found that tungsten has very little tendency to dissolve in molten nickel at 1800°; but can be prepared by melting the nickel in an electric crucible furnace with a carbon electrode, and adding nickel oxide to remove the carbon; then introducing the tungsten, and after all is melted, deoxidizing with magnesium. The f.p. curve with up to 50 per cent. tungsten shows a maximum at 1480° corresponding with **nickel hexadecitatungstide,** $Ni_{16}W$, and one at 1495° corresponding with **nickel hexitatungstide,** Ni_6W.

The former may not be a definite compound. There is a eutectic at 1426° and 2 at. per cent. of tungsten: one at 1435° and 9·2 at. per cent. of tungsten; and one at 1456° and 17 at. per cent. of tungsten. Solid soln. are probably formed with up to 2 at. per cent. tungsten. R. Vogel observed no sign of $Ni_{16}W$, and his equilibrium curves, Fig. 167, are different from those of R. Irmann, Fig. 167. The behaviour of alloys with more than 80 per cent. of nickel is difficult to observe accurately because of supercooling, and alloys with over 50 per cent. of tungsten lose their fluidity and become "pasty" with increasing concentrations of tungsten. Observations were not made above 1600°. The crystallizing temp. of alloys with 0 to 35 per cent. of tungsten rises from 1475° to 1525°, whilst a second, very irregular thermal effect is observed below 900°, becoming steady at 905° with 35 per cent. of tungsten. The maximum crystallization point at 1525° corresponds with the composition Ni_6W. From 35 per cent. of tungsten the crystallization curve falls to 1510° at 47 per cent. of tungsten, this being the limiting composition for complete miscibility. There is a eutectic point at 52 per cent. of tungsten, 1510°, the eutectic consisting of saturated mixed crystals of Ni_6W and tungsten with pure tungsten. The secondary thermal effect which, in alloys containing from 45 per cent. of tungsten upwards, is constant at 905°, appears to be due to the separation of sat. mixed crystals into their constituents Ni_6W and tungsten. The limiting composition for ferromagnetism at the ordinary temp. in the alloys is between 10 per cent. and 20 per cent. of tungsten. The separation of the mixed crystals into their constituents at 905° is probably due to the transformation of the nickel from the β- to the α-form. K. Becker and F. Ebert studied the X-radiograms of the hexitatungstide. V. Adelsköld and co-workers observed that if carbon is present, a complex **nickel tungsten tritacarbide,** Ni_3W_3C, is formed.

The Brinell hardness of these alloys is a minimum with 15 per cent. of tungsten. The tensile strength (kgrms. per sq. mm.) of these alloys decreases rapidly with increasing proportions of tungsten, attaining a minimum with 25 per cent. of tungsten, and then rising just as rapidly. The ductility of nickel, however, is adversely affected by the addition of tungsten, so that only when the tungsten is less than about 18 per cent. can the hot metal be rolled into sheets:

Tungsten	0	5	6	8	11	18	23	32 per cent.
Tensile strength	—	—	45·8	—	43·4	36·1	21·1	49·2
Brinell's hardness	—	144	—	125	107	108	148	288
$R\times10^{-4}$	0·110	—	0·367	—	0·497	0·748	0·960	1·063

W. Kahlbaum and co-workers studied the tensile properties. The electrical resistance, $R\times10^{-4}$ ohm per cm. cube, thus increases almost proportionally with the tungsten content up to 23 per cent. One important use for the alloys is in the manufacture of metal-filament, incandescent lamps exploited by E. W. von Siemens and J. G. Halske, and the Allgemeine Elektrizitätsgesellschaft. W. Rohn studied the thermoelectric force of the alloys against platinum; and C. Sadron, the magnetic properties. J. Trowbridge and S. Sheldon found the sp. magnetism of the alloys to be:

Tungsten	0	1	2	3	6 per cent.
Sp. magnetism	1·05	1·92	1·70	1·75	1·15 c.g.s. units

The alloys are characterized by their resistance to attack by many chemical reagents. Alloys with 6 and 14·3 at. per cent. of tungsten exhibit a maximum resistance to corrosion by acids, and a minimum resistance in the neighbourhood of a eutectic. I. P. Podolsky and N. M. Zarubin studied the action of sulphur vapour; and H. Gruber, the action of hydrogen sulphide between 700° and 1000°. According to R. Irmann, the resistance of nickel to attack by 63 per cent. sulphuric acid is increased four-fold by the addition of 5 per cent. tungsten, and twelve-fold by the addition of 10 per cent. The resistance increases more slowly between 10 and 18 per cent. tungsten, and at 25 per cent. decreases considerably, increasing

again from 30 per cent. Thus, at 90° during 12 hrs.' action, the losses in mgrms. per sq. cm., plotted in Fig. 168, are :

Tungsten	0	5·4	11·1	15·0	18·5	23·5	27·7	32·0	47·8	per cent.
Losses .	33·00	8·52	2·98	1·86	0·80	1·17	2·92	2·13	0·35	

O. Rumschottel found that in the ternary **copper-nickel-tungsten alloys,** the tungsten in the molten alloy separated out on freezing. R. Irmann, however, prepared a series of the ternary alloys, and found that the alloys with W : Cu =3·57 : 21·10 could be reduced 5 per cent. by rolling ; the 4·40 : 33·20 alloys, 8 per cent. ; the 4·98 : 47·01 alloys, 40 per cent. ; and the 8·02 : 39·80 alloys, 70 per cent. The material is hardened by rolling, and it can then be softened by annealing, thus,

Annealed at . .	665°	765°	865°	915°	980°	1080°	1140°	1200°
Brinell's hardness .	275	239	239	229	208	175	175	114

The hardness curve of the alloys has a break at 1140° corresponding with the softening temp. The Brinell's hardness of the ternary alloys is :

2 per cent. W	Copper .	0·0	10·3	20·3	39·1	48·7	per cent.
	Hardness .	145·0	106·2	95·4	110·0	113·9	
5 per cent. W	Copper .	0·0	20·4	31·0	41·9	—	per cent.
	Hardness .	144·0	110·0	92·2	102·6	—	
10 per cent. W	Copper .	0·0	96	19·9	30·1	39·2	per cent.
	Hardness .	109·0	118·2	142·6	137·4	132·1	

The results are plotted in Fig. 169. The cast-rods with Cu : W=40·89 : 4·28 had the tensile strength 35 kgrms. per sq. mm., and the percentage elongation 6·0 ;

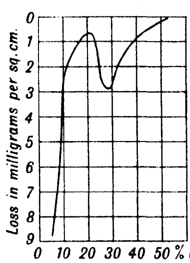


FIG. 168.—The Action of Sulphuric Acid on Nickel-Tungsten Alloys.

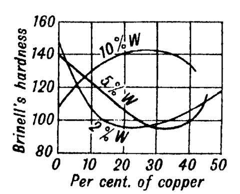


FIG. 169.—The Hardness of the Cu-Ni-W Alloys.

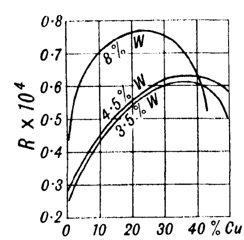


FIG. 170.—The Electrical Resistance of the Ni-Cu-W Alloys.

for the 47·01 : 4·98 alloy, the corresponding values were 47 and 17 ; and for the 39·80 : 8·02 alloy, 39 and 5·6. The ternary alloy with Cu : W=42·9 : 5·09 freezes during the interval 1350° and 1260° ; and the 20·3 : 2·18 alloy during the interval 1372° and 1355°. This is taken to show that solid soln. are formed. J. C. McLennan and C. J. Smithells studied the absorption coeff. for γ-rays. The electrical resistance of the alloy, $R \times 10^4$ ohms per cm. cube, was found to be (plotted in Fig. 170) :

	3·5 per cent. W		4·5 per cent. W			8 per cent. W	
Copper	21·10	45·80	33·00	47·01	47·65	20·99	39·80 per cent.
$R \times 10^4$.	0·557	0·546	0·625	0·603	0·560	0·772	0·609 ,,

R. Irmann represented the corrosion of the ternary alloys represented by the losses in mgrms. per sq. cm. by the action of sulphuric acid under like conditions, by the curves, Fig. 171, and by the data :

2 per cent. W	Copper	0·0	10·3	20·3	39·1	48·7	per cent.
	Loss .	23·20	0·52	0·00	1·57	4·47	
3 per cent. W	Copper	0·0	9·5	20·3	36·2	—	per cent.
	Loss .	20·00	3·17	2·12	2·20	—	
5 per cent. W	Copper	0·0	20·4	31·0	42·9	—	per cent.
	Loss	10·0	2·48	1·62	0·91	—	
10 per cent. W	Copper	0·0	9·6	19·9	30·1	39·2	per cent.
	Loss .	3·00	0·49	1·19	1·00	2·75	

K. Grassmann and E. J. Kohlmeyer studied the copper-tungsten-nickel alloys, and the **copper-tungsten-nickel-tantalum alloys.** The **copper-nickel-zinc-tungsten alloys,** approximating nickel-silver with 1 to 2 per cent. of tungsten, have the trade-name platinoid—say Cu, 60; Ni, 14; Zn, 24; W, 1 to 2. E. S. Sperry described platinoid free from tungsten, and A. M. Fairlie described a platinoid with Cu, 54·0; Ni, 24·77; Zn, 20·42; Fe, 0·47; Mn, 0·15; and Pb, 0·15. O. Rumschottel said that tungsten separates out from the molten liquid obtained by adding nickel-tungsten alloys to copper-zinc alloys. R. Irmann studied the effect of tungsten on the corrodibility of nickel-silver. C. A. Lees said that the thermal conductivity of platinoid at 18° is 0·060 c.g.s. units; 0·058 at 0°; 0·047 at −80°; and 0·042 at −160°. The sp. electrical resistance, R c.g.s. units, was given by J. Dewar and J. A. Fleming:

	100°	18·45°	0·8°	−80°	−100°	−182°
R .	44,590	43,806	43,610	43,022	42,385	41,454

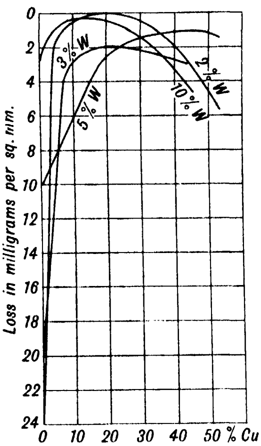


Fig. 171.—The Action of Sulphuric Acid on the Ni-Cu-W Alloys.

The resistance of platinoid, said J. T. Bottomley, is about 1·5 times as great as that of nickel-silver, and the temp. coeff., $0·0_4509$ to $0·0_422$. A. G. Warren and F. Murphy found the e.m.f. of the couple with platinoid and bronze is −15·5 microvolt per degree. M. Maclean found that the e.m.f. of a couple of platinoid wires, one of which was stretched longitudinally, was 0·0910 microvolt per degree difference of temp. between the cold and hot junctions. The current passed from the stretched to the unstretched wire. He found for platinoid:

Total load . . .	250	500	750	1000	1250	1500	1750 grm.
Temporary elongation	0·035	0·071	0·101	0·130	0·160	0·190 per cent.	
Permanent elongation	—	—	—	0·025	0·030	0·035 ,,	
Microvolts per degree.	0·1058	0·1190	0·1330	0·1532	0·1683	0·2177	

P. Ludwik and R. Scheu, B. Jones, and P. Chévenard studied the mechanical properties of the **nickel-tungsten-chromium alloys,** and the alloy with the trade-name *illium,* described by C. T. Knipp and J. L. Hall, is an alloy of nickel and chromium with some tungsten and other elements. P. A. Heller [20] prepared **nickel uranium alloys.**

T. Fleitmann [21] observed that with **nickel-manganese alloys** containing up to 10 per cent. of manganese the working qualities are not destroyed. Alloys were prepared by H. Wedding, W. B. Driver, and M. Basse and M. von Selve. A. Leuchter, and A. N. Campbell described the preparation of the alloys electrolytically. S. F. Schemtschuschny and co-workers studied the f.p. curve, and the result is summarized in Fig. 172. There is an unbroken series of solid soln. with a minimum in the curve at 1030°, and 56 per cent. of manganese. With alloys having 36 to 51 per cent. of manganese, the freezing-point curve shows a break between 790° and 816° indicating that the solid soln. is decomposed with the possible formation of a definite compound. A. D. Dourdine found a flat minimum a little over 1000° with between 56 and 63 per cent. of manganese, which shows peculiarities taken to indicate the formation of a stable and an unstable modification of **nickel manganide,** NiMn. P. I. Gradusoff, A. D. Dourdine, M. von Selve, K. Honda and T. Ishigaki, B. Blumenthal and co-workers, S. Valentiner and G. Becker, and N. B. Pilling and T. E. Kihlgren

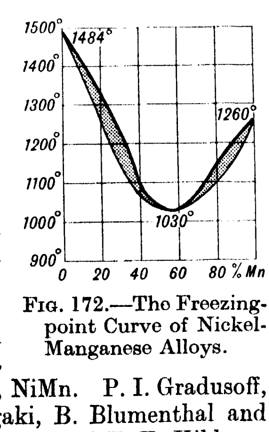


Fig. 172.—The Freezing-point Curve of Nickel-Manganese Alloys.

discussed the constitution of the alloys; A. W. Smith, the thermal conductivities; J. Cournot, the magnetic properties. E. Persson and E. Oehlman studied the X-radiograms—*vide* manganese; and W. Nowacki, and S. Kaya and A. Kussmann, the lattice structure of **nickel tritamanganide,** $MnNi_3$.

W. A. Mudge and L. W. Luff examined the mechanical properties (lbs. per sq. in.) and found:

	0·05		1·89		4·63 per cent. Mn	
	Hot-rolled	An-nealed	Hot-rolled	An-nealed	Hot-rolled	An-nealed
Bakewell hardness .	67·0	60·5	69·0	63·0	77·0	68·0
Proportional limit .	22,800	19,700	25,500	22,000	31,350	25,850
Yield-point . .	33,400	26,750	34,350	27,500	38,550	22,650
Ultimate strength .	77,200	76,850	81,800	80,700	86,500	85,800
Elongation in 2 ins. .	43·7	48·5	39·7	48·9	42·5	46·0 per cent.
Reduction area .	59·5	75·9	63·5	74·2	52·6	72·4 ,,

B. Jones, K. R. Koch and C. Dannecker, and H. J. French and W. A. Tucker discussed the properties of these alloys; M. A. Hunter and J. W. Bacon, the electrical resistance; and W. Rohn, the thermoelectric force of the alloys against platinum. S. Kaya and A. Kussmann found that the Curie point of the nickel-manganese alloys starts at 356°, the value for purified nickel, but is lowered by the addition of manganese until it reaches ordinary temp. with 25 per cent. of manganese. With increasing manganese content, at ordinary temp., there is a distinct increase in the saturation value for small manganese contents, an effect which is still present at the temp. of liquid air. With between 5 and 10 per cent. of Mn, the curve reaches a maximum, which, at ordinary temp., lies about 10 per cent., and at —193° about 20 per cent., higher than the corresponding value for pure nickel. With alloys containing more than about 10 per cent. of Mn, some transformation occurs in the alloy at a temp. between 400° and 600°. An alloy which has been slowly cooled through this temp. range and tempered is more highly magnetic than one which has been rapidly cooled through this stage. With increasing manganese content there is a greater difference between the two states, so that rapidly cooled alloys containing 24 per cent. of Mn have only a fraction of the magnetizability they have if cooled slowly. K. Kreielsheimer, and W. Rohn measured the electrical resistance of a nickel-manganese alloy; and W. Meissner studied the conductivity of the alloys at the temp. of liquid helium. S. Kaya and A. Kussmann, A. Dauvillier, E. C. Stoner, and J. G. Gray found that by previous cooling to —190°, no change occurs in the magnetic properties, and that in this respect they differ from nickel and manganese steels. G. Tammann and E. Vaders studied the electrode potential of **nickel-manganese alloys,** and they found that the solid soln. of the two metals has a limit with 0·5 mol. Ni. O. von Auwers and H. Kühlewein studied the magnetic properties of the alloys. The corrodibility of the nickel-manganese alloys was studied by W. Guertler and T. Liepus.

There are quite a number of more complex manganese-nickel alloys which have been recommended as resistance wires. Amongst the **nickel-manganese-copper alloys** there are *manganin*—Cu, 86·62; Ni, 3·261; Mn, 8·031; Sn, 0·073; Fe, 0·60; more usually, according to W. Jäger and H. Diesselhorst, Cu, 84; Ni, 4; Mn, 12; or, according to K. Feussner and St. Lindeck, Cu, 86; Ni, 2; Mn, 12; or, according to W. B. Driver, Cu, 75; Ni, 20; Mn, 5; or, according to A. M. Fairlie, Cu, 82·12; Ni, 2·29; Mn, 15·02; Fe, 0·57. These alloys were discussed by V. Fischer, A. le Thomas, S. F. Schemtschuschny and S. A. Pogodin, E. S. Sperry and J. B. Rhodes. N. Parravano's study of the ternary system is summarized in Fig. 173, showing the liquidus (continuous) curves, and the solidus (dotted) curves. The system forms solid soln. in all proportions. The preparation of the alloys and also the microstructure of manganin were described by H. Behrens, and R. Vogel. The sp. gr. given by W. Jäger and H. Diesselhorst is 8·44 at 18°. E. Grüneisen found the elastic modulus to be 12,599 kgrms. per sq. mm.

P. W. Bridgman gave for the reciprocal of Young's modulus of manganin, $0{\cdot}72\times10^{-6}$; Poisson's ratio, 0·33; and the cubic compressibility, $0{\cdot}7\times10^{-6}$. D. J. McAdam measured the static, mechanical tests and the fatigue tests of hot-rolled Ni : Cu : Mn (67·51 : 26·23 : 4·31) alloy expressed in lbs. per sq. in. Taking the sample as received, and the same sample after annealing in that order, the results were: Tensile strength, 91,600 and 88,800; torsional strength, 73,400 and 78,300; shearing strength, 65,800 and 60,000; and endurance limit, 39,000 and 37,800. H. Ebert studied the compressibility, and E. Grüneisen obtained $0{\cdot}0_6 81$ for the compressibility coeff., and R. F. Mehl and B. J. Mair obtained a smaller value by calculation from the mixture rule. W. Jäger and H. Diesselhorst found the thermal conductivity to be 0·217 c.g.s. units at 18°, and 0·264 at 100°, so that the temp. coeff. is 2·7 per cent. C. A. Lees gave 0·052 at 18°; 0·050 at 0°; 0·040 at −80°; and 0·035 at 160°. M. A. Hunter and J. W. Bacon, L. Rolla, S. A. Pogodin and E. M. Lekarenko, and A. W. Smith studied the subject. W. Jäger and H. Diesselhorst gave 0·0973 for the sp. ht. at 18°, and 0·1004 at 100°. The time of melting thin fuses was measured by J. A. M. van Liempt and J. A. de Vriend.

The electrical resistance of manganin is high, and the temp. coeff. of the resistance is small. C. Heusler said that the sp. resistance is 41 to 45 microhms per cm. cube, and the temp. coeff. is negative at 16°; K. Feussner and St. Lindeck

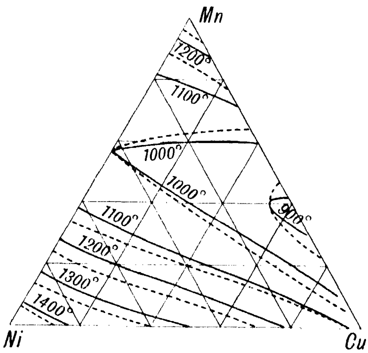


FIG. 173.—Isothermal Curves of the Ternary System: Cu–Ni–Mn.

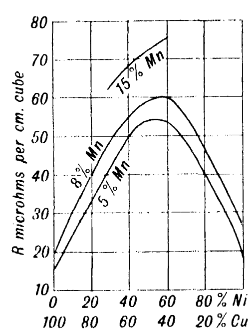


FIG. 174.—The Electrical Resistance of the Cu-Ni-Mn Alloys.

gave 47·7 microhms per cm. cube for the resistance, and the temp. coeff. is −0·00003; a manganin resistance coil of 1 ohm at 18° has a resistance of 1·000050 ohms at 27·5°; it is again 1 ohm at 38°; and 0·999900 ohm at 46°. W. Jäger found that the resistance coils did not change in value over a period of six years. Observations were made by F. E. Bash, M. A. Hunter and A. Jones, W. H. Stannard, Firm Ahler and co-workers, E. L. Nichols, N. B. Pilling, E. L. Lederer, E. Weston, etc. G. Niccolai gave for the resistance in absolute units, R,

	−189°	−100°	0°	25°	100°	125°	400°
R . .	37,937	38,427	38,787	38,832	38,847	38,832	38,258

F. M. Sebast and G. L. Gray found for the resistance R microhms per cm. cube at 20°, and the temp. coeff. α, for the ternary alloys:

5 per cent. Mn	Ni .	0	20	40	50	60	70	80	100 per cent.
	R .	17·9	33·5	50·4	55·1	54·35	50·72	38·8	17·4
	$\alpha\times10^3$	0·17	0·14	0·089	0·085	0·22	1·09	7·39	2·97
8 per cent. Mn	R .	19·7	40·2	54·8	58·1	60·05	55·8	45·8	23·3
	$\alpha\times10^3$	0·32	0·075	0·071	0·088	0·14	0·53	1·85	2·49
15 per cent. Mn	R .	—	—	68·7	70·8	75·3	—	—	—
	$\alpha\times10^3$	—	—	−0·016	+0·025	+0·064	—	—	—

The results are plotted in Fig. 174, and show that the presence of manganese

increases the resistance of the copper-nickel alloys, and an increase in the resistance is accompanied by a decrease in the temp. coeff. An alloy of Cu, 50; Ni, 40; and Mn, 10 has a resistance of about 70 microhms per cm. cube and a zero temp. coeff. at 20°. A. A. Somerville's results for the effect of temp. on the resistance of manganin are summarized in Fig. 175. N. B. Pilling, M. A. Hunter and J. W. Bacon, H. Rolnick, J. Strauss, and S. F. Schemtschuschny and co-workers studied the temp. coeff. of the resistance of manganin; and A. Michels and M. H. Lenssen, the effect of pressure. P. W. Bridgman gave for the resistance at 0°, 1·0000; at 26°, 1·0007; at 50°, 1·0006; at 76°, 1·0002; and at 97°, 0·9995, so that there is a maximum near 30°. He also found the effect of pressure, p, in kgrms. per sq. cm. to be such that the press. coeff. of the resistance R, or (dR/dp)

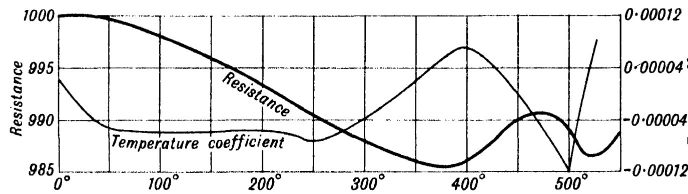


FIG. 175.—The Effect of Temperature on the Resistance of Manganin.

$=0 \cdot 0_5 2325$. A. Lafay gave $0 \cdot 0_5 216$ per kgrm. per sq. cm., and E. Lisell, $0 \cdot 0_5 208$ to $0 \cdot 0_5 213$ for annealed wire and $0 \cdot 0_5 279$ to $0 \cdot 0_5 2338$ for hard-drawn wire. According to E. B. Rosa and H. D. Babcock, the resistance increases with an increase in the humidity of the air, but not so according to W. Jäger and St. Lindeck. The subject was discussed by F. E. Smith. W. E. Williams said that the resistance increases with an increase in pressure. A. Michels and M. H. Lenssen studied the effect of pressure. P. W. Bridgman found that the press. coeff. of the resistance is practically the same at 0°, 25°, 50°, 75°, and 100°, but between 25° and 50° there was an increase of 0·7 per cent. When the wire is subjected to a tensile stress, the observed resistance increases at the rate of $0 \cdot 0_6 571$ per kgrm. per sq. cm.; the corresponding press. coeff. is $0 \cdot 0_5 231$; the tension coeff. for the sp. resistance $-0 \cdot 0_6 60$. H. Rolnick measured the effect of tension on the resistance; and W. H. Sanders and A. P. Carman, the effect of a magnetic field. N. d'Agostino found that the resistance increases 0·01 per cent. in a magnetic field of 6000 gauss. G. Tammann and E. Vaders found that the electromotive force of the cell $Ni \mid 0 \cdot 125M\text{-}MnCl_2 \mid Mn_nNi_{1-n}$ has a break with $n=0 \cdot 5$. M. A. Hunter and J. W. Bacon, E. H. Hall, and N. B. Pilling made observations on the subject.

W. Jäger and H. Diesselhorst found that the thermoelectric force of manganin against copper is 1·6 microvolts at 18° and 1·4 microvolts at 100°; against bronze, A. G. Warren and F. Murphy found 0·36 to 0·52 microvolt per degree; J. Dewar and J. A. Fleming obtained for the e.m.f. E c.g.s. units of the alloy against lead, with the cold junction at 0°, and the hot junction:

	100·1°	50·5°	26·2°	12·6°	−12·7°	−26·4°	−54·1°	−160·6°	−203·1°
E .	13,770	6300	3115	2070	−1010	−2510	−4320	−11,040	−14,130

P. W. Bridgman gave for the e.m.f. of manganin against lead, $E \times 10^6 = 1 \cdot 366\theta + 0 \cdot 000414\theta^2 + 0 \cdot 0000112\theta^3$ volts. M. Maclean found the e.m.f. of a couple of manganin wires, one of which was permanently stretched longitudinally, 0·0693 microvolt, and that the current passed from the stretched to the unstretched wire. He found for manganin,

Total load . .	250	500	750	1000	1250	1500	1750 grms.
Temporary elongation . .	—	0·145	0·260	0·327	0·382	0·427	0·484 per cent.
Permanent elongation . .	—	0·012	0·072	0·120	0·151	0·166	0·193 ,,
Microvolts per degree . .	0·05665	0·06372	0·06272	0·06778	0·06474	0·06474	0·06575

P. W. Bridgman observed that with a couple composed of one branch of uncompressed metal, and the other compressed to a press. p kgrms. per sq. cm., the junctions being at 0°, the thermoelectric force $E\times 10^6$ volts:

	p	10°	20°	40°	60°	80°	100°
$E\times 10^6$	2,000 .	0·026	0·057	0·100	0·146	0·190	0·211
	6,000 .	−0·081	−0·157	−0·300	−0·431	−0·554	−0·673
	12,000 .	−0·158	−0·308	−0·588	−0·846	−1·087	−1·314

M. Aliamet, and F. Peters discussed the use of the copper-nickel-manganese alloys for the manufacture of thermocouples. P. W. Bridgman observed the Peltier effect between uncompressed and compressed metal expressed in $p\times 10^6$ joules per coulomb, to be:

	p	0°	20°	40°	60°	80°	100°
$p\times 10^6$	2,000 .	−0·71	−0·73	−0·74	−0·75	−0·76	−0·77
	6,000 .	−2·27	−2·20	−2·13	−2·12	−2·14	−2·14
	12,000 .	−4·41	−4·28	−4·20	−4·15	−4·13	−4·14

The Peltier effect against lead is $p\times 10^6=(1{\cdot}366+0{\cdot}008280\theta+0{\cdot}0_4336\theta^2)(\theta+273)$ volts. The Thomson effect against lead is $\sigma\times 10^6=(0{\cdot}00828+0{\cdot}0000672\theta)(\theta+273)$ volts per degree, and with compressed and uncompressed metal, expressed in $\sigma\times 10^8$ joules per coulomb per degree:

	p	0°	20°	40°	60°	80°	100°
$\delta\times 10^8$	2,000 .	0·14	0·15	0·16	0·17	0·18	0·19
	6,000 .	1·40	1·08	0·78	0·53	0·28	0·00
	12,000 .	2·46	2·01	1·66	1·39	1·17	1·01

J. Obata studied the Hall effect; and W. Frey gave for the Hall effect, $R\times 10^6$, of manganin, with a field strength of H gauss;

	150°	225°	270°	330°	360°	440°	590°	730°	810°
H . .	4100	4150	4170	4350	4540	4790	4490	4740	4920
$R\times 10^6$.	−569	−554	−522	−473	−455	−432	−437	−483	−460

J. Cournot studied some non-magnetic alloys of nickel and manganese; E. Englert, some magnetic alloys. N. d'Agostino said that the electrical resistance decreases with transverse magnetization. K. Feussner and St. Lindeck observed that manganin acquires an oxidation film at 100°, and at a red-heat, the superficial manganese is wholly oxidized so that the resistance of the wires is altered: J. W. Richards added aluminium to the **copper-nickel-manganese alloys,** and obtained what he regarded as one of the hardest of the light alloys. N. B. Pilling studied the resistance of these alloys; and J. Obata, the Hall effect. H. Goldschmidt prepared alloys with chromium by the thermite process. W. Guertler and T. Liepus studied the corrodibility of the nickel-manganese-copper alloys; M. S. van Dusen and S. M. Shelton, the thermal conductivity; L. J. Wood, the X-ray structure and microstructure; and W. Rosenhain and co-workers. K. F. Bingham, and E. D. Gleason, the properties of the **nickel-manganese-copper-aluminium alloys.**

A. F. Cronstedt,[22] the discoverer of nickel, prepared some **nickel-iron alloys** in 1754, and he said that "amongst the metals proper, iron has the greatest friendship for nickel." T. Bergman, and A. and C. R. Aikin said that iron and nickel unite in all proportions to form alloys as ductile and magnetic as iron itself. Alloys were also described by W. L. Austin, W. P. Barba and H. M. Howe, W. R. Barclay, H. Bessemer, G. H. Billings, F. Bohny, H. C. H. Carpenter, G. Charpy, J. Escard, M. Faraday and J. Stodart, R. Flechner, T. Fleitmann, G. Grard, L. Guillet, W. Heym, J. B. Hoblyn, A. L. Holley, J. B. C. Kershaw, W. A. Lampadius, J. von Liebig, F. H. Mason, P. D. Merica, T. Moore, P. Oberhoffer, F. Osmond, J. Percy, F. Peters, O. J. Steinhart, F. J. Taylor, J. L. F. Vogel, O. Vogel, F. B. H. White, E. H. Williams, D. Wilson, D. N. Witman, T. D. Yensen, etc. Some alloys were made by M. Faraday and J. Stodart, and later examined by R. A. Hadfield. Alloys of iron and nickel were patented by T. W. Dodds,

J. W. Furness, J. F. Hall, S. S. Hickling, A. Jacobsen, W. Longmaid, C. McKnight, H. Marbeau, J. Martineau and H. W. Smith, A. Parkes, M. Poole, and H. Schneider. T. W. Hardy and H. N. Bleakney described the direct production of the alloy from Sudbury ore. J. Wharton observed an alloy accidentally formed on the hearth of a nickel smelting furnace. P. Berthier said that the two metals easily alloy together in all proportions. M. Rubach, A. Weiske, and O. L. Erdmann observed that wrought iron frequently contains traces of nickel. J. Riley said that alloys can be made in any good open-hearth furnace working at a fairly good heat. No special care is required in working the charges since the composition is easily and definitely controlled. Nearly all the nickel will be found in the charge; very little is lost in the slag. Any scrap produced in hammering, rolling, shearing, etc., can be remelted in making another charge, without loss of nickel. For alloys with a high proportion of nickel, H. Wedding recommended the addition of 0·14 per cent. of magnesium shortly before pouring. F. Cirkel prepared nickeliferous iron from nickeliferous pyrrhotite; W. H. Greene and W. H. Wahl obtained alloys with 50 per cent. of nickel by melting ferrosilicon with nickel oxide; and M. Rudeloff said that in preparing ingots, 20 grms. of aluminium per 20 kgrms. of metal should be added to alloys rich in iron, and 10 grms. of magnesium per 20 kgrms. of metal, to alloys rich in nickel. The preparation of the alloys was also described by R. A. Hadfield, W. Venator, S. Kern, A. W. Richards, H. D. Hibbard, etc. E. Thilges prepared alloys from sulphide ores. T. Fujiwara tried refining the alloy in the acidic open-hearth furnace. D. and H. E. Hanson made alloys by melting purified iron and nickel in aluminium crucibles, heated in an atm. of nitrogen. A. N. Campbell obtained alloys by the electrolysis of soln. of the appropriate sulphates; the subject was investigated by H. J. Blikslager, K. Engemann, T. Fujiwara, S. Glasstone and T. E. Symes, F. W. Küster, B. Leech and F. Hammond, F. Marschak and co-workers, R. W. W. Sanderson, E. von Sjöstedt, L. E. Stout and J. Carol, and G. Töpfer. R. Kremann and co-workers did not find an increased press. of hydrogen made any perceptible difference to the deposit of iron and nickel obtained electrolytically from a mixed soln. of ferrous sulphate alone, the resulting iron contained less occluded hydrogen with hydrogen at a high press. than at a low press. Alloys of iron and nickel were prepared by J. W. Andrews, P. Benvenuti, D. H. Browne, G. Bruni and M. Amadori, J. Escard, J. Garnier, S. Glasstone and co-workers, N. V. Hybinette, F. Krupp, H. Lange, A. Leuchter, C. P. Madsen, R. M. Major, F. H. Mason, O. L. Mills, H. Ottinger, M. Stern, J. H. White, D. Wilson, C. H. Worsnop, and T. D. Yensen. R. W. W. Sanderson, R. Kreeman and co-workers, E. Raub and E. Walter, D. Stepanoff and co-workers, and L. E. Stout and J. Carol studied the electrodeposition of nickel-iron alloys.

Some occurrences of natural nickel-iron alloys have been reported. A small proportion of nickel occurs in many samples of native iron (*q.v.*), and some meteorites contain a high proportion. W. Skey found a nickeliferous iron approximating $FeNi_2$ in the drift of the George river emptying into Awarua Bay, New Zealand, and he called it **awaruite.** G. H. F. Ulrich supposed that it is derived from neighbouring serpentines or peridotites. R. A. A. Johnston observed grains of a similar alloy from Yukon; and A. Sella, in the auriferous sands of the Elvo, Piedmont. The grains resemble platinum; they are malleable, and magnetic, and have a sp. gr. of 7·8. W. H. Melville obtained pebbles of an alloy approximating Fe_2Ni_5 in the placer gravel of a stream in the Josephine and Jackson counties, Oregon; and the mineral was called **josephinite.** G. S. Jamieson also obtained josephinite from Smith River, Del Norte Co., California. G. C. Hoffmann obtained an alloy approximating Ni_3Fe from the auriferous sands of Frazer River, British Columbia, and he called it **souesite**—after F. Soues. The so-called **octibbehite,** Fe_2Ni_3, is a nickel-iron alloy from Octibbeha, Missouri, found by W. J. Taylor to contain 36·67 Fe, 59·69 Ni, 0·40 Co, 0·90 Cu, and 0·10 P; while S. Meunier called the alloy Fe_2Ni from Santa Catharina, Brazil, **catharinite.**

The term **ferro-nickel** is applied to alloys of nickel and iron in contrast with the term **nickel-steel,** which is an alloy steel. The terms are sometimes confused, and some prefer to restrict the term ferronickel to alloys of iron with over, say, 25 per cent. nickel. Steels with from 1·5 to 95 per cent. nickel are sold in commerce, and the nickel-steels are employed for a great variety of purposes—gun tubes and other parts of guns, pneumatic hammers and air-drills, turbine blades, gas-engine valves, ignition tubes, boiler tubes, sparking plugs, axles, shafts, steering knuckles, gears, and various parts of automobiles, aeroplanes, machinery, and various constructional purposes when the metal is subject to severe stresses. The so-called nickel-steel resistance wires employed for electric heaters, toasters, cookers, etc., contain, say, 24 to 30 per cent. nickel, and some have special trade terms—*e.g.*, *tico*, *climax*, etc. The alloy *indilation* has 64 per cent. of iron and 36 per cent. of nickel—with impurities 0·06 C; 0·68 Mn; and 0·09 Si. The uses of the nickel-steels were discussed by J. Riley, B. Simmersbach, S. Kern, F. L. Sperry, C. E. Guillaume, A. Ledebur, R. A. Hadfield. High nickel alloys are also sold under special names, and some are made with almost any required thermal expansion. Thus, the so-called **invar steels** on account of their having a small, in many cases negligible, coeff. of thermal expansion are used in the manufacture of measuring and other instruments; for chronometers and other clockwork, tapes for geodetic measurements, etc. The thermal and magnetic properties are discussed in connection with the general subject. A sample of the commercial alloy **elinvar** had 0·84 C; 1·5 Mn; 11·1 Cr; 0·14 Si; 32·7 Ni; 3·9 W; and 49·8 Fe; and **modulvar,** 0·16 C; 0·18 Mn; 0·12 Cr; 0·14 Si; 34·9 Ni; and 64·5 Fe. The following description is from the circular of the Bureau of Standards, *Invar and related Nickel Steels* (Washington, 1916):

Invar is a nickel-steel containing about 36 per cent. nickel together with about 0·5 per cent. each of carbon and manganese, with metallurgically negligible quantities of sulphur, phosphorus, and other elements. It is made either in the open-hearth furnace or by the crucible method. It melts sharply at about 1425°. Some 200° above its m.p., invar is supposed to consist of a homogeneous solid soln. of iron, nickel, and carbon. Below 200°, and at a temp. dependent on its history and exact composition, it undergoes a reversible transformation of such a nature that for any sample the transformation may be incomplete. This condition of thermochemical instability gives rise both to slowly changing and quickly changing values for its physical properties—changes which are particularly manifested in the expansion. The alloy invar can be forged, rolled, turned, filed, and drawn into wires, and it takes a beautiful polish, giving an excellent surface on which fine lines may be ruled. In general, it should be worked slowly. It will withstand without spotting the corrosive action of water, even when immersed for several days. Its sp. gr. is about 8·0 grms. per c.c.; its electrical resistivity is of the order of 80 microhms per cm. cube, or about 8 times that of pure iron; and its temp. coeff. of electrical resistance about 0·0012 per degree. It is ferromagnetic, but becomes paramagnetic in the neighbourhood of 165°. The mean coeff. of linear expansion between 0° and 40° is of the order of one-millionth for the ordinary invar, and samples have been prepared with even small negative coeff.; the amount of carbon and manganese present appear to exercise considerable influence on the expansion. Small quantities have been manufactured with a coeff. of $(+0{\cdot}028-0{\cdot}00232\theta)10^{-6}$, equivalent to a change in length of 0·4 mm. in 1 kilometre between 0° and 20°. This was for an alloy containing 0·006 per cent. carbon and 0·39 per cent. manganese, the other elements being negligible. Above 200°, the expansion of invar is nearly that of Bessemer steel. Invar is subject to changes in length due to "after effects" following cooling from a high temp., and to changes in length following even slight alterations in temp. For example, at 15°, the elongation per metre is 0·07 to 0·08μ per day after forging and 0·03μ after annealing to 40°. After a long rest at room temp. (10° to 20°) the contraction setting in after bringing the metal to a higher temp. is completed in about one-half-hour at 100° and only after several days at 40°. The range of transitory length variations following temp. changes is given approximately by the formula $\delta l/l=-0{\cdot}00325\times10^{-6}\theta$, which holds for temp. between 0° and 100°. Invar also gradually elongates with time, forged and drawn material behaving somewhat differently in this respect, so that there is a determinable, seasonal correction to be applied to its length when used as a standard. This effect may be reduced, but not entirely eliminated, by special heat treatments consisting in an annealing process extending over several weeks carried out at successively decreasing temperatures. Invar also shows marked magnetostriction phenomena, or changes of length accompanying changes in strong magnetic fields. The invar from a single melt will not, in general, be of absolutely uniform

properties throughout, the expansion variations not being more than $\pm 0{\cdot}03 \times 10^{-6}$, so that, in determining lengths to one part in ten million, it appears safe to use the same expansion formula for all the pieces from a given melt. The mechanical properties are about as follows: Tensile strength, 35 to 60 kgrms. per sq. mm., or 50,000 to 85,000 lbs. per sq. in.; elastic limit, 5 to 21 kgrms. per sq. mm., or 7000 to 30,000 lbs. per sq. in.; elongation, 40 to 50 per cent.; reduction of area, 40 to 64 per cent.; scleroscopic hardness, 19; and Brinell hardness, 160.

The alloy **platinite** contains about 46 per cent. of nickel and 0·15 per cent. of carbon; it has a coeff. of thermal expansion the same as that of platinum. These and similar alloys can be used in place of platinum for sealing into glass as the leading-in wires of electric lamps, although a compound wire with a 38 per cent. nickel-steel core encased in copper, or coated with platinum, is used for that purpose. The alloys are also used for the delicate mountings of special lenses to avoid the risk of optical strains with variations of temp. The so-called **permalloy** is a special magnetic alloy with about 80 per cent. of nickel, which after a suitable heat-treatment has a magnetic permeability at a small field strength which is many times greater than any hitherto known. There is a range of these alloys—with over 30 per cent. of nickel—which are capable of attaining a high magnetic permeability. They are used in the construction and operation of submarine cables, etc. The properties were discussed by L. Houllevigue, also in connection with the general subject. L. W. McKeehan studied the atom grouping in permalloy; H. D. Arnold and G. W. Elmen, T. D. Yensen, E. M. Deloraine, and A. E. Kennelly, the magnetic properties of permalloy; L. W. McKeehan, the magnetostriction of the alloy.

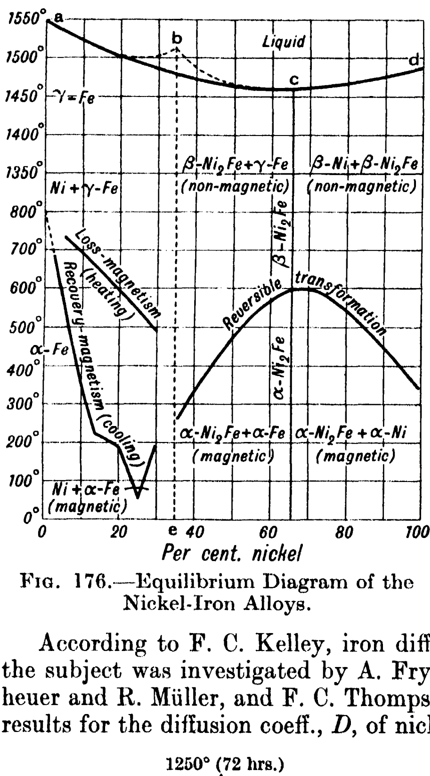


FIG. 176.—Equilibrium Diagram of the Nickel-Iron Alloys.

According to F. C. Kelley, iron diffuses into nickel, but not nickel into iron; the subject was investigated by A. Fry, N. Agéeff and M. Zamatorin, P. Bardenheuer and R. Müller, and F. C. Thompson and W. H. Dearden. W. van Drunen's results for the diffusion coeff., D, of nickel into iron are:

1250° (72 hrs.)			1300° (72 hrs.)		
Depth cm.	Nickel per cent.	$D\times10^4$	Depth cm.	Nickel per cent.	$D\times10^4$
0·00325	42·8	0·533	0·00425	46·2	1·540
0·00875	25·7	0·299	0·01475	25·8	0·785
0·01325	9·4	0·169	0·03275	3·4	0·529

Observations on the joint diffusion of nickel and chromium were also recorded. D. H. Browne found a cavity in a copper-nickel matte lined with brilliant, tin-white, magnetic crystals of the composition Fe_8Ni_9. L. Guillet found that a nickel coating on steel is absorbed at about 450°. T. Peczalsky, and J. Fetchenko-Tschopiwsky also studied the cementation of iron by nickel.

W. Guertler and G. Tammann found that the f.p. curve of the nickel-iron alloys consists of two branches, *ab*, and *bcd*, Fig. 176. The curve *bcd*, extending from 35 to 100 per cent. of nickel, has a minimum at *b*. R. Ruer and L. Schuz, and W. Fraenkel and G. Tammann, however, showed that under ordinary conditions this curve is continuous for the two elements, γ-iron, and β-nickel, form a continuous series of solid soln. The curve has then a shallow minimum, and the

liquidus and solidus curves virtually coincide. The curve showing the dependence of the transformation temp. on the composition of the solid soln. has a break. The temp. of solidification, and the temp. of the loss and recovery of magnetizability are:

Nickel	0	20	40	60	80	100	per cent.
Solidification	1545°	1495°	1489°	1480°	1468°	1484°	
Loss of magnetizability	755°	590°	310°	566°	568°	330°	
Recovery of magnetizability	750°	205°	290°	567°	568°	325°	

R. Ruer and L. Schuz agree generally with the results of C. E. Guillaume, and F. Osmond on the temp. of the magnetic transformations, but they place the boundary between the reversible and non-reversible alloys at 29 per cent. of nickel; the maximum of the reversible transformation at 618°, and the minimum of the f.p. curve at 1435°. Both these temp. lie near to 70 per cent. of nickel, and are assumed to correspond with the existence of a **nickel hemiferride,** Ni_2Fe. There is a slight lag in the reversible magnetic transformation with heating and cooling. R. Ruer and L. Schuz's observations on the electrical conductivity of these alloys give no indication of the presence of such a compound; but those of M. Peschard on the magnetic properties do, and they also indicate the existence of Ni_2Fe_3, as well as of Fe_2Ni. Some physical properties—observed by L. R. Ingersoll, M. Peschard, P. Chévenard, P. Weiss and G. Foëx, D. Hanson and J. R. Freeman, D. and H. E. Hanson, K. Honda and H. Takagi, R. Ruer and L. Schuz, T. Kase, W. Guertler and G. Tammann, O. Boudouard, A. Dumas, F. Osmond, F. Osmond and G. Cartaud, A. Schulze, G. Gossels, and C. Benedicks—show critical values at about 35 per cent. of nickel, and hence the assumption of a **nickel diferride,** NiF_2.

D. Hanson and J. R. Freeman found that the freezing of the alloys begins along *ABCD*, Fig. 177; and that δ-iron separates out over the range *AB*. Alloys

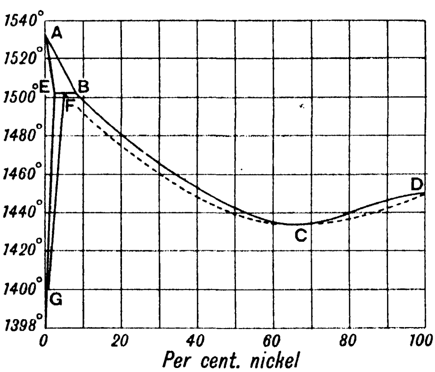


Fig. 177.—The Solidification of the Nickel-Iron Alloys.

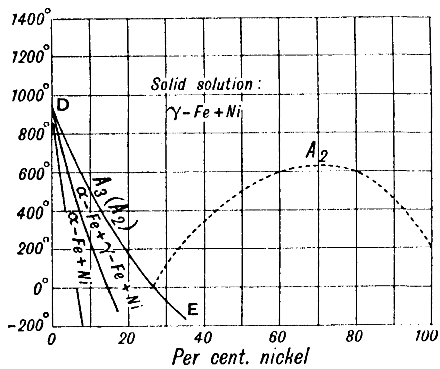


Fig. 178.—The Equilibrium Diagram of the Solid Iron-Nickel Alloy.

between *B* and *D* consist, when just solid, of a series of solid soln., with a minimum f.p. at *C*, approximately 65 to 70 per cent. of nickel. The alloys rich in iron undergo a transformation below the liquidus, and δ-iron changes into γ-iron, and the transformation is represented by the broken line *GEB*. The portion *GE* can be regarded as representing the raising of the δ- to γ-transformation temp. of iron by nickel. Only 3 per cent. of nickel raises this temp. 100°. The point *E* represents the maximum solubility of nickel in δ-iron, and along *EB*, δ-iron of the composition *E* reacts with liquid of the composition *B* to form γ-iron of the composition *F*. Nickel is more soluble in γ-iron than in δ-iron. The point *F* is only approximate. The solidus *AEFCD*, dotted in the diagram, has not been determined. It is very close to the liquidus line, especially in the region *B* to *D*. The hardness of the alloys shows no discontinuity in the region *C*. The alloys with 5 to 50 per cent. of nickel all consist of a single constituent after solidification.

The equilibrium diagram was also studied by H. Benneck and P. Schafmeister, W. Broniewsky and J. Smolinsky, U. Dehlinger and H. Bumm, L. Grenet, J. F. Hall, K. Honda and S. Miura, S. Iguchi, T. Kase, S. A. Pogodin, F. Sauerwald and F. Fleischer, and R. Vogel. T. Kase's thermal diagram of the solid region is shown in Fig. 178. The curve *DE* is plotted from the observed values of the Ar_3-arrests. T. Kase gave for the different arrests :

Ni	0	1	8·40	10·0	21·37	27·80	33·40	40·01	99·63 per cent.
Ac_2	800°	790°	730°	—	—	50°	170°	360°	360°
Ar_2	775°	770°	570°	—	—	40°	155°	340°	345°
Ac_3	910°	870°	740°	710°	620°	—	—	—	—
Ar_3	890°	840°	610°	520°	200°	—	—	—	—
$Ac_{3,2}$	—	—	—	—	—	470°	370°	—	—
$Ar_{3,2}$	—	—	—	—	—	−20°	−130°	—	—

T. Kase showed that the liquidus curve is on the iron side in agreement with D. Hanson and J. R. Freeman, but not in agreement with R. Vogel; for the peritectic reaction between the solid soln. and melt occurs in the range of composition from about 3·5 to 8 per cent. of nickel, and then the liquidus curve gradually falls, whereas R. Vogel stated that the peritectic reaction occurs in the range between 6 and 35 per cent. of nickel. E. C. Bain, and M. R. Andrews studied the X-radiograms, and these indicate that nickel dissolves in α-iron to the extent of 25 to 30 per cent., and there is a region when the space-lattices of the nickel and iron overlap. This is complicated by the fact that when quenched, the γ-iron lattice appears and the overlapping is shifted towards the iron end of the series. H. Benneck and P. Schafmeister discussed the $\delta \rightarrow \alpha$ transformation.

E. Howard demonstrated in 1802 that nickel is a constant component of meteoric iron. The meteoric nickel-iron alloys contain up to about 27 per cent. of nickel, and thus belong to the group of solid soln. ranging up to 35 per cent. of nickel and occur in the equilibrium diagram to the left of the line *ae*, Fig. 176. The meteoric nickel-irons often show the Widmanstätten figures, and also Neumann's lines—*vide* **12**. 66, 17. C. von Reichenbach studied the Widmanstätten figures of meteorites, and called the three kinds of nickeliferous iron, recognized by P. Partsch, a *trias*, and designated the broad lamellæ of the Widmanstätten structure Balkaneisen or **kamacite**—from κάμαξ, a pole or shaft, in allusion to the lath-like or beam-like outline of the plates on sectioned surfaces; and F. Heide and co-workers observed that the crystals have a body-centred, cubic lattice, with a=2·859 A. This constituent is darkened on etching or on oxidation; it consists of hexahedral crystals containing about 6 per cent. of nickel. The thin lamellæ or small rounded particles were called *Bandeisen* or **tænite**—from ταινία, a band. This crystalline constituent contains about 33 per cent. of nickel, and it is but slightly attacked on etching. The third constituent was called *Fulleisen* or **plessite**—it takes up the space between the kamacite lamellæ, and it is regarded as a more or less finely-divided, mechanical mixture of kamacite and tænite. The structure of meteoric iron was discussed by N. T. Belaiew, O. B. Böggild, L. H. Borgström, A. Brezina, O. Buchner, K. Busz, P. Clausen, O. A. Derby, T. Hodge-Smith, L. A. Kulik, A. Lacroix, J. Leonhardt, W. J. Luyten, G. P. Merrill, L. F. Navarro, H. H. Nininger, G. T. Prior, L. J. Spencer, P. N. Tschirvinsky, R. Vogel, E. A. Wülfing, etc.

F. Berwerth, and E. Pfann thus describe the general properties of these three constituents. *Kamacite* contains about 6·5 per cent. of nickel; it crystallizes in the cubic system. According to J. Leonhardt, the X-radiogram of kamacite corresponds with a cubic, body-centred lattice with the parameter a=2·84 A. Kamacite has a well-defined cubic cleavage, and in all its forms shows polysynthetic twin lamellæ parallel to the faces of an icosatetrahedron. These twin striations which are shown by cleavage or etching are Neumann's lines—*vide* iron. The forms of kamacite vary from large masses to the finest grains in plessite or in granular meteoric iron. In the transitions, it appears in short thick columns, or

in plates according to thickness, coarse, medium, or fine lamellæ in the octahedral meteoric irons. The orientation of kamacite in meteoric iron was studied by J. Young. *Tænite* is more nickeliferous than kamacite, and it contains between 13 and 35 per cent. of nickel. G. Tschermak found the tænite from the Ilimæ meteorite to be a segregation of nickel-iron in iron. S. W. J. Smith assumed that tænite is a eutectic of kamacite in a nickel-iron crystal of a different type. Tænite is almost developed in thin lamellæ closely adhering to the kamacite plates in band-like fringes of yellowish, bright, metallic lines which are very prominent on etched surfaces. In plessite, it is reduced to films and very small grains. *Plessite* is a eutectoidal mixture of kamacite and tænite. It occupies the interspaces between the plates or bands of the structure. Plessite has been 17 and 18 per cent. of nickel. The differences in colour, lustre, and behaviour on etching enable the different constituents to be easily diacuminated on a polished and etched surface. When they occur together, they make up the crystalline patterns known as Widmanstätten figures. There are thus only two homogeneous constituents. The higher the nickel content of the meteorite, the more tænite it contains, and if the proportion of nickel is below 6 or 7 per cent., no tænite is present, and the meteorite contains only kamacite. When only kamacite is present, the meteoric iron can usually be split rather easily along the cubical surfaces, and it is then often called *cubic meteoric iron.* When over 7 per cent. of nickel is present, kamacite appears, it forms lamellæ oriented according to the octahedral surfaces, and the Widmanstätten structure appears. The meteoric iron is then called *octahedral meteoric iron.*

F. Osmond and G. Cartaud constructed a tentative equilibrium diagram for meteoric iron. The alloy is assumed to have been formed as a homogeneous solid soln. of γ-iron, and β-nickel, and that on cooling, kamacite segregates out when the proportion of nickel is below 13 per cent.; tænite when the proportion exceeds 44 per cent. nickel; and a mixture of kamacite and tænite with intermediate proportions of nickel. A solid soln. with 30 per cent. of nickel furnishes plessite, which can be regarded as a eutectoidal mixture of kamacite and tænite. F. Rinne's modification of the equilibrium diagram of F. Osmond and G. Cartaud is shown in Fig. 179. The proposed adjustment in Fig. 180, by D. and H. E. Hanson, is

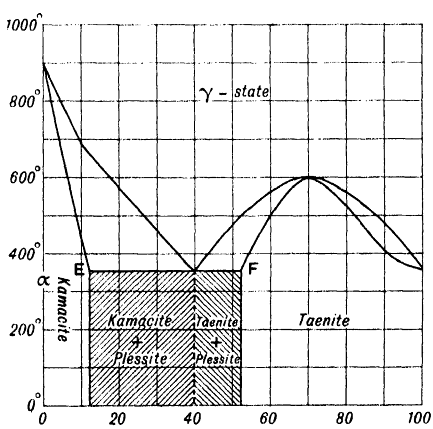


FIG. 179.—Equilibrium Diagram of the Iron-Nickel Alloys.

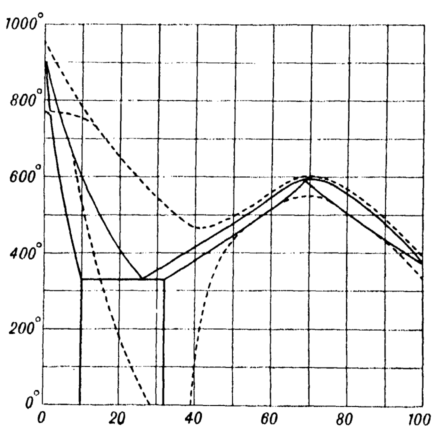
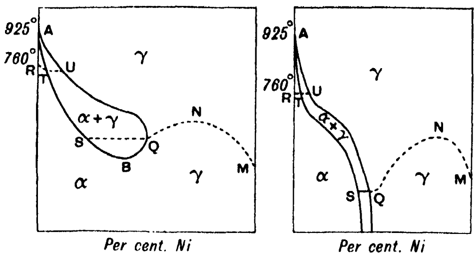


FIG. 180.—Equilibrium Diagram of the Iron-Nickel Alloys.

based on their experimental work. The thin dotted lines show the transition points obtained from the thermal curves and electrical conductivity measurements; and they indicate the deviation of the transformation points from their probable equilibrium temp. L. Grenet considered that these diagrams will want

considerable modifications in the region of the solid soln. before they can be accepted as close approximations. He considered that diagrams resembling Fig. 181 or 182 are more in accord with the facts. Fig. 181 relates to the existence of limiting states between the α- and β-phases. B corresponds with a critical temp. and composition, analogous to the limiting state between the liquid and vapour phase in a mixture of two liquids. AQB denote the composition of the γ-phase saturated with the α-phase; $BSTA$, the composition of the α-phase saturated with the γ-phase; RTU and $MNQS$, curves of the magnetic transformations of the α- and γ-phases. Fig. 182 is considered to be the better approximation since it includes the decided variation in the direction of the equilibrium curves of α and γ corresponding with the variation of magnetism in the γ-phase. Here, ACB represents the region of the coexistence in equilibrium of the α- and γ-phases; RTU, the curve of magnetic transformation of the α-phase; and $MNQS$, the curve of the magnetic transformation of the γ-phase. Assuming that the δ-phase is the same as the α-phase, the transformations on cooling are the δ- to the α-phase, with evolutions of heat at 1400°; and the γ- to α-phase with an evolution of heat at 925°.



FIGS. 181 and 182.—Equilibrium Diagrams of the Nickel-Iron Alloys.

Returning to the diagram of F. Osmond, and F. Rinne, Fig. 179, if the cooling is slow enough, it is assumed that the cooling alloy will split up into distinct phases; the sluggishness, lag, or hysteresis of the segregation accounts for the failure of A. Daubrée, S. Meunier, W. Fraenkel and G. Tammann, H. C. Sorby, and J. E. Stead to obtain alloys exhibiting the structure of meteoric iron. J. E. Stead, indeed, was so impressed with the importance of slow cooling that he said that several hundred years would probably be required for one experiment; and C. Benedicks was able to obtain a segregation of an alloy with 12 per cent. nickel into two phases with 60 hrs.' cooling. The one constituent appeared as a matrix and it behaved like kamacite, and the other constituent was present in a smaller proportion, it was more resistant to acids, and it behaved like tænite. The two constituents were not uniformly distributed. In some parts, the two constituents were closely associated as in plessite. The kamacite plates were clearly oriented, forming intersections corresponding with octahedral surfaces and imparting the Widmanstätten structure. Annealing the nickel-iron alloy at 350° produced no change in 42 hrs., but 3 hrs. at 490° caused a recrystallization. Hence, the line EF, Fig. 179, is probably near the truth. An alloy of 6·7 per cent. of nickel and about 0·3 per cent. of phosphorus treated similarly, furnished a product with kamacite, and isolated patches of tænite, so that the nickel was not all dissolved. The solubility limit E, Fig. 179, is possibly a little less than 7 per cent. The fracture was analogous to that of cubic meteoric iron. C. Benedicks said that in some parts of the alloys, there are some spots where the segregation has not had time to become discernible under the microscope, and he added that these spots are analogous to troostite—or cementite—ferrosol—representing a colloidal state containing ultramicroscopic particles. The solid colloidal system may thus be called *tænite-ferrosol*. M. Peschard said that thermal and magnetic observations indicate that meteorites are in physicochemical equilibrium, but that artificial ferronickels are metastable.

W. Fraenkel and G. Tammann subjected samples of the Damara and Toluca meteorite to extensive heat-treatments and concluded that the homogeneous soln. is the stable form. R. Vogel regarded these constituents as unstable at ordinary temp., and said that by suitable annealing, they are converted into a homogeneous

γ-solid soln. This, however, does not explain the facts. He also assumed that the observed structure of meteorites does not correspond with states of equilibrium for *irdische Bedingungen*. It is here assumed that the homogeneous solid soln. is an unstable form possessing a tremendous lag or hysteresis, otherwise, it would be necessary to assume, as C. Benedicks laconically observed, that the laws governing the structure of metals are different in different parts of the universe. The observations of C. Benedicks, and R. Ruer and L. Schuz on the electrical resistance of iron-nickel alloys, slowly cooled, are in agreement with the assumption that iron containing not too small a proportion of nickel, segregates into two constituents when slowly cooled under industrial conditions. According to F. Osmond and G. Cartaud, some experiments by A. Dumas indicated that *par recuit ou écrouissage, on pourrait obtenir un commencement de segrégation qui rapprocherait un peu les alliages industriels des météorites*. D. and H. E. Hanson also observed that the decomposition of austenite can take place over a wide range of composition into a duplex mass, of which the two constituents are assumed to be kamacite and tænite. This segregation, however, did not occur under the conditions of their experiments, when 35 per cent. of nickel was present. Such alloys remained homogeneous after all treatments. J. Leonhardt found that the kamacite in meteoric iron has a body-centred, cubic lattice with $a=2{\cdot}84$ A. —J. Young gave 2·870 A. M. R. Andrews, A. Osawa, A. O. Jung, and L. W. McKeehan observed that the iron-nickel alloys form two phases. M. R. Andrews showed that the X-radiograms indicate that the space-lattice of alloys with 0 to 22 per cent. of nickel is a body-centred cube, and alloys with 30 to 100 per cent. of nickel, a face-centred cube, while alloys with 25 to 27 per cent. of nickel have a mixture of the body-centred and face-centred cubic lattices—*vide infra*. J. Young gave for the face-centred cubic lattice of tænite the parameter $a=3{\cdot}590$ A. L. W. McKeehan found that the parameters $a\times10^8$ cms. for the body-centred and face-centred cubic lattices, and the calculated sp. gr., are as follow (the bracketed data are based on a few faint lines):

Nickel		0	10	30	35	45	55	75	95	100 per cent.
a	Face	2·872	2·873	2·885	—	—	—	—	—	—
	Body	(3·629)	(3·586)	(3·618)	3·595	3·602	3·581	3·567	3·531	3·510
Sp. gr.	Face	7·775	7·718	7·787	—	—	—	—	—	—
	Body	(7·712)	(8·034)	(7·898)	8·069	8·063	8·245	8·424	8·774	8·853

There is a difficulty about the right side of the equilibrium diagram, Fig. 179. When F. Osmond constructed the diagram, it was generally assumed that the magnetic change corresponded with the appearance of another allotropic phase. F. Wever, however, showed that no change in the space-lattice is revealed by the X-radiograms, and P. Chévenard, M. Peschard, and T. Kase assumed that no change of phase occurred. C. Benedicks pointed out that if no change of phase occurs, the segregations which occur about 350°, and peculiarities in the expansion curves observed by P. Chévenard, and T. Kase, and in the electrical resistance curve observed by H. le Chatelier, are difficult to explain. The absence of a change in the space-lattice does not exclude the existence of two phases because it would be also necessary to show that no discontinuous change occurs in the lattice parameter. T. Kase obtained a plain Widmanstätten, or martensitic structure after a prolonged heating of the iron-nickel alloy, and also a 0·054 carbon-iron (no nickel) alloy at 1000°. This temp. is too high for the splitting up of a homogeneous alloy into two phases. C. Benedicks explained this by assuming that the portions of the alloy which crystallize first are richer in nickel, and obtain an orientation which is influenced by the γ-matrix, and that an exceedingly long time is required to produce the homogeneity required at that temp. for F. Osmond's equilibrium diagram to be in accord with facts. Even with invar alloys with 36 per cent. of nickel the two phase structure is shown by the local, deep etching pits which form throughout the metal, and which are often more concentrated at definite places where more iron goes into soln. These pits are supposed to be due to kamacite.

Even on an unetched surface, a darker, finely-divided structure is apparent in red light. The micro-etching pits of invar have the same general characteristics as those observed in a larger proportion in a 30·5 per cent. alloy, where a two-phase microstructure is known to occur. The subject was discussed by M. von Schwarz, E. L. Reed, J. A. M. van Liempt, T. Sato, and E. Namba.

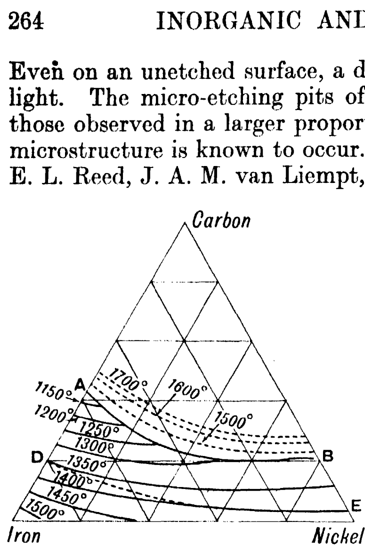


FIG. 183.—Isothermal Lines of the Liquidus Curve in the System: Fe–Ni–C.

The nickel-carbon system was discussed in connection with the carbides—**5**. 39, 20. T. Kase obtained the isothermal curves, Fig. 183, for the liquidus curves of the ternary system; *AB* is the projection of the eutectic curve; and *DE* represents the solubility of carbon at the eutectic temp. J. H. Andrew and D. Binnie observed that the nickel-steels freeze at a lower temp. than plain carbon steels; the f.p. depends on the nickel content. The m.p. or the solidus curve occurs at approximately the same temp. as plain carbon steels containing the same proportions of carbon. There is less segregation, or a greater homogeneity, with the nickel-steels since, firstly, the liquidus and solidus lines come nearer to one another with respect to temp. than they do with plain carbon steels; and secondly, the peritectic transformation may be obliterated. F. Osmond found that in the presence of 0·16 per cent. of carbon, the effect of nickel on the transformation points of iron is as follows:

Nickel	0	0·27	0·94	3·82	7·65 per cent.
Ar_3-arrest	820°	775°–765°	755°–745°	—	—
Ar_2-arrest	750°	715°–695°	695°–685°	645°–635°	—
Ar_1-arrest	660°	645°–635°	625°–615°	565°–550°	515°–505°

so that with increasing proportions of nickel, the transformation zones are rapidly lowered, and coincide when about 4 per cent. of nickel has been added. The effect of nickel on the transformation temp. is shown graphically in Fig. 184, and the effect of nickel on the magnetic transformations resemble the results given in Fig. 184. The transformations on the heating and cooling curves are so different with steels containing less than 25 per cent. of nickel that the alloys are called *irreversible steels*; steels with higher proportions of nickel show only a slight lag on the heating and cooling curves, and they are accordingly called *reversible steels*.

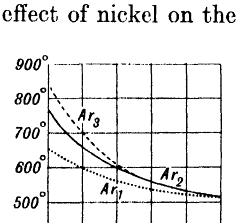


FIG. 184.—The Effect of Nickel on the Transformation Points of Steel.

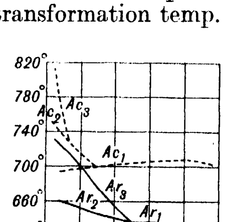


FIG. 185.—The Effect of Carbon on the Transformation Points of Nickel-Steel.

A. McWilliam and E. J. Barnes' observations on the effect of carbon on the transformation temp. of a 3 per cent. nickel alloy are summarized in Fig. 185, where the dotted (smoothed) lines refer to the arrests on the heating curves, and the continuous (smoothed) lines refer to arrests on the cooling curves. Note the range of temp. between the Ac_1- and the Ar_1-arrests—*vide supra*, Figs. 184 and 185. H. C. H. Carpenter and co-workers also found the carbon change or A_1-arrest of steel to be materially affected by nickel, and the transition temp. becomes a range of temp. which increases with increasing proportions of nickel. The carbon change point is depressed to such an extent that with 20 per cent. of nickel it is practically suppressed. This effect of nickel is the predominating factor in determining the microstructure, and incidentally the mechanical properties of the nickel-carbon alloys. O. Boudouard

measured the effect of carbon and nickel on the transition temp. by a thermoelectric process, and the results are summarized in Table XI. H. Meyer found

TABLE XI.—THE TRANSFORMATION POINTS OF NICKEL-STEELS.

Percentage composition		Transition points		Percentage composition		Transition points	
C	Ni	Heating	Cooling	C	Ni	Heating	Cooling
0·070	2·23	860°, 775°, 725°	830°–710°	0·800	2·20	705°	695°
0·125	5·23	770°–695°	710°	0·776	4·90	675°	625°
0·125	7·13	690°–660°	650°	0·815	7·09	665°	560°
0·132	10·10	675°–650°	575°	1·050	9·79	625°	560°
0·125	12·07	640°–610°	420°	0·760	12·27	625°	560°
0·110	15·17	620°	360°	0·796	15·04	590°	560°
0·176	20·40	600°	300°	0·800	20·00	560°	560°
0·160	25·85	510°	175°	0·790	25·06	515°	560°
0·120	30·00	510°	175°	0·810	29·96	515°	560°

the effect of nickel on the beginning of the separation of ferrite at the Ar_3-arrest to be:

Nickel . .	1·0	2·0	3·0	4·0	5·0	6·0 per cent.
Lowering of Ar_3 .	32	65	100	140	185	235 ,,

K. Honda and S. Miura found that the difference between the beginning and end of the A_3-transformation is real, and is increased by increasing proportions of the nickel as illustrated by Fig. 186, with armco iron, and heating or cooling at the rate of 2° per minute, Ac_3-change begins at 860° and ends at 905°, whilst the Ar_3-change begins at 889° and ends at 850°. Hence, they conclude that the A_3-transformation with iron alloys takes place through a range of temp. and should be regarded as a point. O. L. Roberts and W. P. Davey found that the Ac_3-transition temp. of alloys with

Nickel .	0	1·04	2·78	4·27	11·73	13·21 per cent.
Tr. temp. .	907°–910°	820°–815°	720°–715°	660°–655°	525°–520°	520°–515°

The Ac_3- and Ar_3- arrests do not coincide; the fractional lowering of the Ac_3-point is greater for the first 10 per cent. of nickel than it is for larger proportions. Below the Ac_3-arrest, the alloys are all body-centred and cubic, and above that temp., face-centred and cubic. R. R. Abbott, F. H. Allison, J. A. Andrew and H. A. Dickie, J. W. Donaldson, W. Haufe, A. Merz, H. Scott, G. J. Sizoo and C. Zwicker, H. Döpper and H. J. Wiester, and M. J. Stutzman studied the Ac_1-range in these steels. T. Kase represented the effect of nickel on the Ar_1-arrest by Fig. 187. This temp. falls at first gradually, and then rapidly as the proportion of nickel increases, but it is almost independent of the content of carbon. A. Sauveur supposed that the Ar_1-arrest is lowered by increasing proportions of carbon, but this is said to be only apparent, since in high nickel-steels, the phenomenon is complicated by a stepped transformation causing apparently a transformation at a lower temp. The A_2-arrest in iron-carbon alloys is nearly constant, irrespective of the carbon content; but if nickel is added to iron, the $A_2(A_1, A_3)$-arrest of the alloys is rapidly lowered with increasing proportions of nickel. If the proportion of carbon is kept constant, the Ac_2-point for alloys with a constant proportion of nickel first falls, and then remains constant as the carbon increases as shown in Fig. 188. The $Ar_2(Ar_1, Ar_3)$-arrest

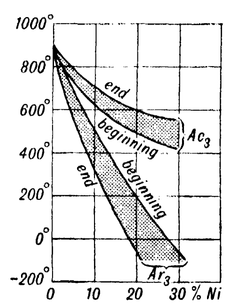


FIG. 186.—The Upper and Lower Limits of the A_3-transformation.

is also affected by the nickel in a similar way, but in a more marked degree, as shown in Fig. 189. When the $Ar_1(Ar_2, Ar_3)$-point is lowered between 500° and 150°, the transformation occurs in two steps usually denoted by Ar′ and Ar″. This phenomenon was discussed by K. Honda and T. Kikuta, K. Sasakawa, L. Guillet and co-workers, and J. Challansonnet—*vide* nickel-vanadium steels.

K. Schichtel and E. Piwowarsky found that nickel lowers the solubility of carbon in liquid iron. With over 15 per cent. nickel, every additional unit of nickel decreases the solubility of carbon in the molten metal at all temp. by 0·045 unit. The f.p. of the metastable eutectic in the iron-carbon series rises 1150° to 1240° as the nickel rises from 0 to 32 per cent., whilst the carbon content decreases from 4·25 to 3·10 per cent. The addition of silicon to iron-nickel alloys or of nickel to iron-silicon alloys counteracts to some extent the reduction of the solubility of carbon caused by the nickel or the silicon originally present; the extent of this action varies with the relative proportions of the alloying elements and with the temperature being very slight at high temperatures with alloys containing much nickel or silicon.

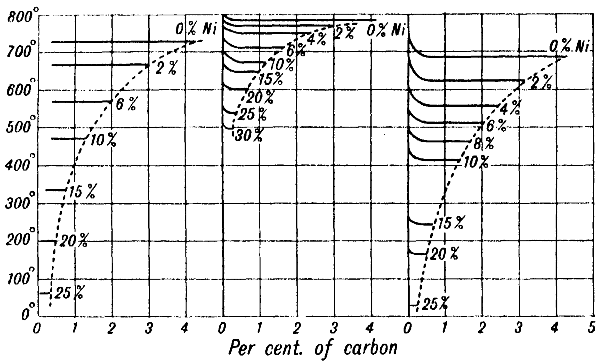


FIG. 187.—The Effect of Nickel on the Ar_1-arrest.

FIG. 188.—The Effect of Nickel on the $Ac_2(Ac_1, Ac_3)$-arrest.

FIG. 189.—The Effect of Nickel on the $Ar_1(Ar_2, Ar_3)$-arrest.

According to S. Iguchi, the Ac_1-arrest in irreversible steels depends on the content of nickel, but not on that of carbon, and the Ar_1- and Ar_2-arrests gradually decrease as the carbon content increases. T. Kase found that the $Ar_{1,\ 3}$-arrest falls gradually as the nickel content increases, but it is almost independent of carbon. The solubility of carbon in the high nickel steels is almost constant—0·25 to 0·30 per cent. In this case, the A_2-arrest is lowered by 15° to 20° owing

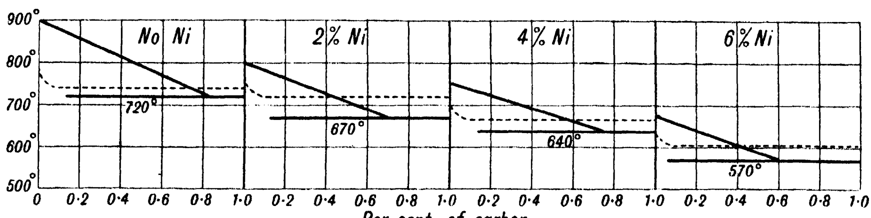


FIG. 190.—The Merging of the Ar_1, and Ar_3-arrests in the Iron-Nickel-Carbon Alloys.

to the dissolved carbon, provided the proportion of nickel is constant. The steels with about 30 per cent. of nickel, when once cooled in liquid air, showed the stepped transformations on heating and cooling. They are the Ac_2-, and $Ac_{3,\ 2}$-, and the Ar_2-, and $Ar_{3,\ 2}$-points for the constituents of alloys having the face-centred and body-centred cubic lattices. The phenomenon is not considered to be due to a transformation of a carbide. L. W. McKeehan followed the variations in the space-lattice of the iron-nickel alloys.

J. J. A. Jones studied the range of the Ar_1-arrest in nickel-steels. T. Kase observed that the Ar_1- and Ar_2-transformations of the iron-carbon alloys occur at

a constant temp., irrespective of the proportion of contained carbon, while the Ar_3-arrest falls rapidly with carbon, and reaches a constant temp. above 0·85 per cent. carbon. T. Kase found that as the proportion of nickel increases, both the A_3- and A_2-arrests in the iron-nickel alloys fall, and coincide at 5 per cent. of nickel on cooling, and at 10 per cent. of nickel on heating. If carbon is also present, the A_1-arrest is similarly affected by nickel. The results are illustrated by Fig. 190. The Ar_3- and Ar_1-arrests coincide at a concentration of about 2 per cent. nickel and 0·80 per cent. carbon at 670°; about 4 per cent. nickel and 0·76 per cent. carbon at about 640°; and about 6 per cent. nickel and 0·6 per cent. carbon at about 570°. This means that the concentration of the carbon at which the eutectoidal transformation occurs gradually increases with increasing proportions of nickel.

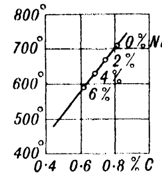


FIG. 191.—The Effect of Increasing Proportions of Nickel on the Proportion of Carbon in the Eutectoid.

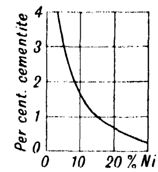


FIG. 192.—The Domain of the Existence of Cementite in Nickel-Iron-Carbon Alloys.

E. Söhnchen and E. Piwowarsky found that nickel displaces the solubility curve of carbon progressively towards the iron-side of the equilibrium diagram, that is, nickel reduces the solubility of carbon in iron almost linearly. Nickel also depresses the eutectoid transformation temp. According to T. Kase, the A_0-arrest at 215° on cooling is not affected by the proportion of nickel, but its existence is usually limited only to alloys containing a certain amount of the metal, for the effect of nickel on the iron-carbon alloys is to graphitize the cementite. The A_0-arrest can be detected in steels containing 0·1 per cent. of carbon. The quantity of carbon combined in the steel diminishes as the nickel content increases, and the amount of cementite gradually decreases, Fig. 192, up to about 25 per cent. nickel, at which about 0·6 per cent. of carbon is dissolved in the solid state. In steels containing more than 10 per cent. of nickel, the lowered, stepped A_1-transformation makes the A_0-transformation indistinct thermally. The equilibrium diagram was also studied by G. J. Sizoo and C. Zwikker, and P. D. Merica.

T. Kase constructed a portion of the equilibrium diagram for the ternary system: Fe–Ni–C, Fig. 193. He found that the carbon-nickel system has a eutectic at 1318°, and 2·22 per cent. of carbon; and that the solubility of carbon in nickel is about 0·55 per cent. at the eutectic temp., and 0·25 per cent. at room temp. In the ternary system: Ni–Fe–C, there is no ternary eutectic, but there is a binary eutectic of a solid soln. consisting of iron-nickel and carbon. In Fig. 193, $ABB'A'$, $AA'DD'$, and $BB'CC'$ represent the concentration-temperature planes for the binary systems Fe–Ni, Fe–C, and Ni–C respectively. $ABFE$ represents the liquidus surface

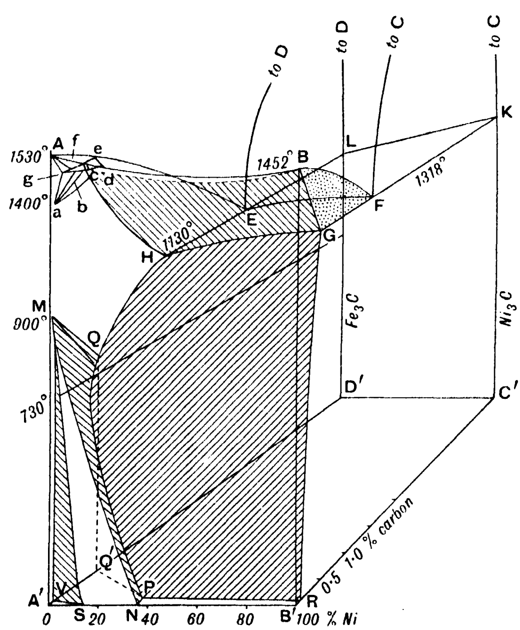


FIG. 193.—Portion of Equilibrium Diagram for the Ternary System: Fe–Ni–C.

along which the ternary austenite, having its composition indicated on the solidus *ABGH*, separates out, and *CDEF* represents the primary surface of the solid soln. of cementite and nickel carbide. The curve *EF*, starting at the eutectic *F* of the Ni–C-system, at 1318°, and ending at the eutectic *E* of the Fe–C-system, at 1130°, represents the eutectic line of the ternary system along which the solid soln. *GH*, and carbide simultaneously crystallize. The eutectic surface *GFKLEH* shows the beginning of the eutectic crystallization; the surface representing the ending of the same crystallization is obtained by drawing a horizontal line between *GH* and *KL*. Primary austenite and the melt exist in the zone *ABGHEF*, and primary carbide and melt, in the zone *CDEFKL*. The surface *GHQPR* represents the solubility of the carbide or carbon in austenite; *MQPN*, the primary surface of the α-solid soln. and the intersection, *QP*, of these two surfaces is the eutectoid or A_1-line of the system. Above these surfaces, there is a homogeneous solid soln., or austenite, and below them, a heterogeneous mixture consisting of two or three of the following: α-solid soln., austenite, and carbide. The presence of nickel in the ternary alloys facilitates the decomposition of the carbides, so that as the proportion of nickel increases, free cementite gradually decreases, and the alloys containing more than 30 per cent. of nickel consist of a mixture of the solid soln. of iron and nickel, and graphite, provided the rate of cooling is normal. The space *MSVA'* represents a homogeneous α-solid soln. consisting of iron, carbon, and nickel; while *MV* denotes the solubility curve of carbon in iron, and *MS*, that of nickel in iron.

In the iron–carbon system, the A_4-arrest, at about 1400°, is raised as the quantity of carbon increases, and at 1487° a peritectic reaction occurs, along the line *gfe*. In the iron–nickel system a similar reaction occurs at 1500°, along the line *bcd*. In the ternary system the corresponding reaction occurs along the line *cf*. The reaction is univariant in the ternary system, while a similar change is invariant in the binary system. No marked change in the diagram for the ternary system occurs except an increase of one degree of freedom. The peritectic temp. gradually falls from *c* to *f*. The surface *Ade* is the liquidus, and *Abg*, the solidus for the δ-solid soln. Along the curve *cf*, the melt *de* reacts with the δ-solid soln. *bg*, forming the γ-solid soln. *cf*. The δ-solid soln. on the surface *abg* is in a state of equilibrium with the γ-solid soln. on the surface *acf*. That is, the melt and δ-solid soln. coexist in the zone *Adegb*; the δ-solid soln. exists in the zone *Abga*; the δ- and γ-solid soln. coexist in the zone *acfgb*; and melt and γ-solid soln. coexist in the zone *BcfEFGH*. V. N. Svechnikoff studied the γ-phase.

P. Dejean found that steels containing 0 to 10 per cent. of nickel are pearlitic and give an arrest *A*, Fig. 194; those with 10 to 25 per cent. of nickel are martensitic and give an arrest *B*; with higher proportions of nickel, the steel is austenite —*cf.* manganese steels. E. Gersten observed that the mol. heat of formation of manganese carbide, Mn_3C, is 12·9 Cals.; of iron carbide, Fe_3C, −15·6 Cals.; and of nickel carbide, Ni_3C, −394·07 Cals. This means that the nickel carbide is very unstable, and in agreement with A. Carnot and E. Goutal's observations, is not likely to be found in steel. G. B. Waterhouse reported the presence of the complex carbide $FeNi_3C$, but this has not been confirmed. L. Guillet observed that nickel in cast iron favoured the precipitation of graphite, and in this manner acted like silicon, and aluminium. The pearlite also becomes more emulsified, eventually assuming the state of the so-called troostosorbite; W. H. Hatfield likewise observed that the addition of nickel favoured the precipitation of free carbon in cast iron, and 3 per cent. renders the pearlitic carbide unstable. The subject was studied by H. M. Boylston,

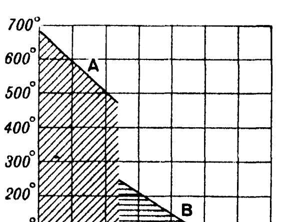


FIG. 194.—The Constitution of Nickel-Steel.

S. J. E. Dangerfield and co-workers, G. Delbart and E. Lecœuvre, A. B. Everest and co-workers, J. Galibourg, W. Guertler, D. Hanson, D. M. Houston, A. Merz and F. Fleischer, S. W. Parker, E. Piwowarsky and W. Freytag, M. J. Stutzman, H. Thaler, and H. Wentrup and W. Stenger. The energetic action of nickel in dissociating the carbide was emphasized by A. McWilliam and E. J. Barnes, and they found that in hypoeutectoidal steels free carbon is precipitated by drastic annealing. F. Roll found that nickel favours the decomposition of carbide in cast iron; and V. N. Krivobok, that it favours the formation of pearlite. K. Schichtel and E. Piwowarsky observed that nickel reduced the solvent power of iron for carbon, and K. Schichtel's solubility curves, *SE*, are indicated in Fig. 193. The effects of nickel on the proportion of carbon in the eutectic, and on the eutectic temp., are shown in Fig. 196; and Fig. 197 shows the parts of carbon precipitated

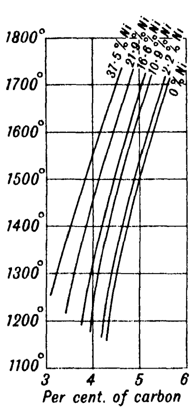


FIG. 195.—The Effect of Nickel on the Solubility Curve of Carbon in Iron.

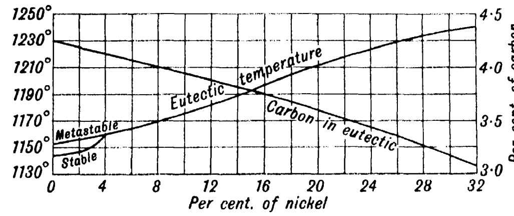


FIG. 196.—The Effects of Nickel on the Eutectic Carbon, and the Eutectic Temperature.

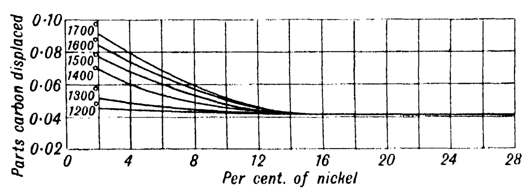


FIG. 197.—The Parts of Carbon Precipitated by the Introduction of each part of Nickel at Different Temperatures.

for each part of nickel introduced at different temp. Observations were also made by T. Kase, L. Thiery, A. Labo, H. J. Schuth, E. Piwowarsky, A. Michel and P. Bénazet, and A. B. Everest. The cementation of nickel-steel was studied by F. Giolitti and F. Carnevali—*vide* **12.** 66, 10. T. Kase's observations on the effect of nickel on the combined carbon in the eutectic alloy of iron and 4·3 per cent. carbon are summarized in Fig. 198 when cooled at a normal rate. Analogous results were obtained for a hypoeutectic alloy, and for alloys quenched from the molten state in an iron mould, and then annealed at about 1000°. As the proportion of nickel increases, the proportion of combined carbon at first rapidly diminishes, and then gradually, until, with 30 per cent. nickel, only 0·25 to 0·30 per cent. of dissolved carbon remains. Thereafter the solubility of carbon in high nickel alloys is almost constant—0·25 to 0·30 per cent. A. B. Everest and co-workers found that nickel and silicon, separately or jointly, tend to graphitize about 40 to 60 per cent. of carbon in an iron-carbon alloy. The graphite produced by nickel is in general finer than that produced by silicon and the addition of nickel to a silicon-iron tends to refine the graphite, as well as to produce a finer pearlite, rendering it sorbitic. J. O. Arnold and A. A. Read observed only iron carbide in the nickel-steels; they said that steels with 13 per cent. of nickel contain Fe_7Ni which they regarded

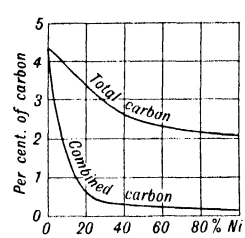


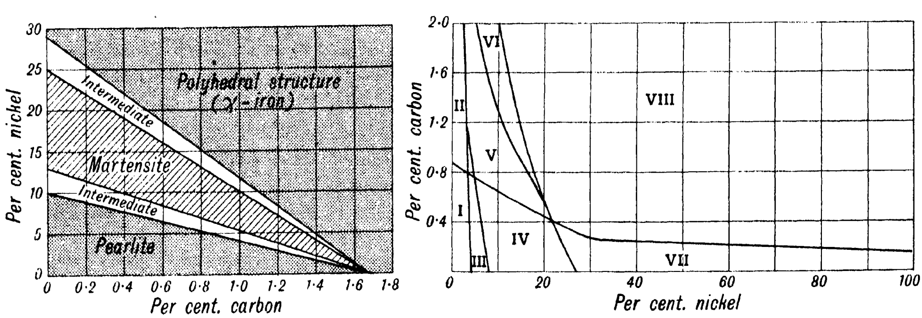
FIG. 198.—The Effect of Nickel on the Dissolved Carbon in the Eutectic Alloy of Iron and 4·3 per cent. Carbon.

as "one of the most remarkable compounds in the metallurgy of iron." The solid soln. of nickel in the iron has a greater solvent power for iron carbide than has iron alone, and nickel-martensite is accordingly more stable than iron-martensite; and with a high nickel content, the solid soln. forms well-defined polyhedral crystals. Structurally, nickel-steel may contain iron carbide as pearlite or cementite; nickel-ferrite; nickel-martensite; and nickel polyhedra which may show cleavage or gliding planes. On annealing, the martensitic and pearlitic structures are formed. According to G. B. Waterhouse, the pearlite of nickel-steel has 0·7 per cent. of carbon. F. Osmond observed that nickel-steels containing

	Percentage of carbon		
	0·12	0·25	0·80 per cent. nickel
Pearlite (and ferrite) . .	0–10	0–7	0–5 ,, ,,
Martensite and α-iron . .	10–12	7–10	5–7 ,, ,,
Martensite	12–20	10–15	7–10 ,, ,,
Martensite and γ-iron . .	20–27	15–20	10–15 ,, ,,
Polyhedra of γ-iron . .	>27	>20	>15 ,, ,,

D. M. Houston found that nickel in grey cast-iron is a pearlite builder and it enables the proportion of combined carbon to be controlled. The effect of nickel on cast iron, etc., was studied by M. Ballay, O. Bauer and K. Sipp, H. Birnbaum, O. Bornhofen and E. Piwowarsky, H. M. Boylston, F. B. Coyle, S. J. E. Dangerfield and co-workers, J. W. Donaldson, A. B. Everest, W. T. Griffiths, D. M. Houston, T. Kawai, C. McKnight, P. D. Merica, E. Piwowarsky, R. S. Poister, E. L. Reed, W. E. Remmers, A. Rys, M. Schmidt and O. Jungwirth, H. A. Schwartz, J. S. Vanick, M. Waehlert, T. H. Wickenden, T. H. Wickenden and J. S. Vanick, and J. G. R. Woodvine.

L. Guillet studied the microstructure of nickel-steel, and he observed that the results are summarized by the diagram, Fig. 199. T. Kase gave Fig. 200 for the



FIGS. 199 and 200.—The Constitution of Nickel-Steels.

structure of the Fe-Ni-C alloys. There are eight regions: I, with pearlite and ferrite; II, with pearlite and cementite; III, with ferrite, martensite, and troostite; IV, with martensite and austenite; V, with martensite, austenite, and cementite; VI, with martensite, austenite, and graphite; VII, austenite; and VIII, with austenite and graphite. W. Giesen also found the three types of L. Guillet exemplified by steels with

Carbon	0·15	0·3	0·95 %
Pearlite and γ-iron .	0–13	0–10	0–6·5 %
Martensite . . .	13–33	10–31	6·5–23 %
γ-iron . . .	>33	>31	>23 %

The alterations in structure depend on the proportions of nickel and carbon which are present. Annealing for 6 hrs. at 1000° had no appreciable influence on the samples with γ-iron and pearlite, though there was in some cases a slight tendency

to form martensite. L. Guillet concluded that the quenching of pearlitic nickel-steels produces results analogous to those obtained with carbon steels, except that the increase in the tensile strength and elastic limit are greater with nickel-steels than with ordinary steels. Quenching is practically without effect on martensitic steels, but if a little ferrite is present, the tensile strength and elongation increase. Quenching reduces the tensile strength and elongation in the case of steels with a little γ-iron ; in the ordinary γ-iron steels, quenching produces a distinct softening, particularly if the metal has been subjected to stresses. Steels in the immediate neighbourhood of the martensitic range are transformed to martensite on quenching, and in consequence, the tensile strength and elastic limit increase, while the elongation and resistance to shock decrease. Annealing softens all nickel-steels with the exception of those containing γ-iron which are on the border-line of the martensitic steels. When a pearlitic steel containing 0·12 per cent. of carbon and 7 per cent. nickel is case-hardened, it may become martensitic at the surface as the proportion of carbon in the surface layer rises to 0·80 per cent. A. B. Everest and co-workers represented the structure of nickel-silicon cast iron by Fig. 201. The area (1) contains pearlite and the austenite-cementite eutectic ; (2) pearlite, proeutectoidal cementite, and graphite ; (3) pearlite and graphite ; (4) sorbite and graphite ; (5) martensite and graphite ; (6) martensite, austenite, and graphite ; and (7) austenite and graphite. J. O. Arnold said that nickel does not form a true steel having 100 per cent. pearlite. The cementation of nickel-steels was studied by A. Sauveur and G. A. Reinhardt, L. Guillet, and D. Hanson and J. E. Hurst—*vide* the cementation of iron and steel. H. Scott found that nickel has only a slight effect on the transformation of martensite to troostite ; and E. Scheil examined the effect of a load on the transformation of austenite to martensite.

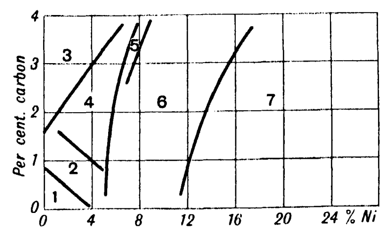


FIG. 201.—The Constitution of Nickel-Silicon-Iron Alloys with 3·5 per cent. Carbon as Cast.

D. H. Browne said that the **colour** of steel becomes higher with increasing proportions of nickel. The 3·5 per cent. nickel-steels do not perceptibly differ in appearance from simple steels ; with 10 per cent. nickel, the colour of the steel is noticeably lighter ; and, at 18 per cent., the steel has a soft, silvery whiteness. With higher percentages of nickel, the colour begins to darken so that steels with 25 and 30 per cent. of nickel are duller and less lustrous than those with 18 per cent. The **texture** of the 18 per cent. nickel-steels is smoother and closer grained than alloys with a higher proportion of nickel. J. Riley observed that molten nickel-steel is more fluid than ordinary steel, it is steady in the mould, it sets more rapidly than ordinary steel, and it is homogeneous. The ingots are clean and smooth on the outside, but those richest in nickel are a little more piped than ingots of ordinary mild steel. There is also less liquation of the metalloids in ingots of nickel-steel. No special care is needed in reheating ingots for hammering or rolling except when over 25 per cent. of nickel is present. If the steel has been properly made, and rightly proportioned, it will hammer and roll well. R. A. Hadfield said that the addition of nickel does not confer soundness, and in the entire absence of manganese, it is not easy to produce sound and readily forgeable bars. The ingots are inclined to be red-short. The addition of aluminium, silicon, or magnesium is necessary for the production of sound castings. The alloys are not susceptible to ordinary **welding.** T. Fleitmann obtained evidence of a welding action at a welding heat when plating iron with nickel by pressure between rollers. E. Piwowarsky, J. Challansonnett, E. Piwowarsky and co-workers, A. Campion, E. Merica, A. B. Everest and co-workers, C. F. Burgess and J. Aston, D. M. Houston, and J. Galibourg discussed the working properties of the iron-nickel alloys : A. B. Everest and co-workers observed that with cast iron, containing

silicon, the addition of 5 per cent. of nickel made the metal hard and unmachinable owing to the formation of martensite; this condition persisted with up to 18 per cent. of nickel, when the alloys became austenitic, soft, and non-magnetic. This is most marked when the alloy contains 20 per cent. of nickel and 1·3 per cent. of silicon. Beyond 20 per cent. of nickel, the alloys remained soft, but they became increasingly magnetic. In the presence of high silicon, more nickel is required to change the matrix through sorbite and martensite than when the silicon is low. Silicon thus masks the effect of nickel. Annealing at the proper temperature, most of the unmachinable alloys can be machined owing to the tempering of the martensite. The nickel-silicon irons are unstable on heating, but not so much as ordinary silicon irons. In high nickel alloys, graphite is precipitated from austenite which tends to become martensitic. According to R. A. Hadfield, the **fracture** of steels having about 0·16 per cent. of carbon and 0·27 per cent. of nickel, showed a mild, open grain like wrought iron; with 0·51 per cent. of nickel, the fracture was fibrous; with 1·92 per cent., the fracture was mild and tearing; with 5 per cent., fine, close, and granular; with 11·39 per cent., dry and harsh; with 24·5 per cent., a close, hard grain, and with 29·07 and 49·65 per cent., the fracture was granular, and it had a slight yellow tinge. A. Schrader and E. Weiss observed no crystal twinning in the metal. H. Meyer discussed the colloidal state; T. Fujiwara, the segregation; and H. Bühler and E. Scheil, the quenching stresses.

The **space-lattices** have been previously discussed, and F. C. Blake and co-workers, M. R. Andrews, F. Kirchner, A. Westgren and A. E. Lindh, J. Young, R. Forster, A. O. Jung, L. W. McKeehan, R. W. Drier, Z. Nishiyama, K. Iwase and N. Nasu, W. Borchers and J. Ehlers, and J. H. Long and co-workers studied the atom grouping in these alloys. A. Westgren and G. Phragmen found that the side of the elementary cube of a 25 per cent. nickel-steel with 0·24 per cent. of carbon was a=3·56 A., when water-quenched from 1000°; while a 22·3 per cent. nickel-steel with 1·18 per cent. of carbon had a=3·64 A. In agreement with analogous observations with carbon steels, the introduction of carbon increases the space-lattice. According to O. L. Roberts and W. P. Davey, the lattice parameters, a, at ordinary temp. of alloys with

Nickel .	0	0·87	1·04	2·78	4·27	11·73	13·21 per cent.
a . . .	2·858	2·864	2·866	2·851	2·849	2·848	2·846 A.

A. Osawa found the X-radiograms of the nickel-iron alloys show that there is a heterogeneous range between alloys with about 25 and 30 per cent. of nickel in which both the body- and face-centred lattices are present—*vide supra*. The results showing the effect of nickel on the lattice parameter a or iron for samples I annealed at 1150°, and II immersed once in liquid air, are:

Nickel . . .		5·21	14·41	29·0	32·64 per cent.
$a\times10^8$ I	Body-centr.	2·865	2·866	2·873	2·875
	Face-centr.	—	—	3·600	3·597
$a\times10^8$ II	Body-centr.	2·865	2·870	2·875	2·872
	Face-centr.	—	—	—	3·599
Sp. gr. I		7·8777	7·9062	7·9808	8·1028
Sp. gr. II		7·8795	7·9001	7·9447	8·0662
Calculated austenite I		—	3·0	39·8	100·0
Calculated austenite II		—	0·0	22·2	81·6
Nickel . . .		41·21	63·94	85·58	100 per cent.
$a\times10^8$ I	Body-centr.	—	—	—	—
	Face-centr.	3·592	3·582	3·549	3·520
$a\times10^8$ II	Body-centr.	—	—	—	—
	Face-centr.	3·593	3·584	3·548	2·523
Sp. gr. I		8·1445	8·6536	8·6536	8·8989
Sp. gr. II		8·1487	8·3378	8·6587	8·8981

Similarly, for samples of nickel-steel, made from steel with 0·8 per cent. of carbon for which a=2·863×10⁻⁸ cm. for the body-centred lattice, and 2·865 for the face-

centred lattice, F. Wever and P. Rütten found that the lattice parameter of γ-iron with carbon in solid soln. expands linearly 0·006 to 0·007 A. per atom. of carbon; and A. Osawa obtained a similar result with nickel-steels. This is illustrated by Fig. 202. H. Perlitz discussed the distance apart of the atoms; and G. Wassermann, the orientation of the crystals.

Nickel		2·37	10·70	20·30	25·19 per cent.
$a \times 10^8$ I	Body-centr.	2·764	2·885	2·876	—
	Face-centr.	—	3·610	3·618	3·610
$a \times 10^8$ II	Body-centr.	2·865	2·880	2·875	2·880
	Face-centr.	—	—	3·612	3·615
Sp. gr.	I	7·844	7·856	8·020	8·002
	II	7·843	7·817	7·925	7·939
Nickel		40·20	60·93	80·56	99·60 per cent.
$a \times 10^8$ I	Body-centr.	—	—	—	—
	Face-centr.	3·608	3·591	3·558	3·528
$a \times 10^8$ II	Body-centr.	—	—	—	—
	Face-centr.	3·608	3·588	3·559	3·530
Sp. gr.	I	8·067	8·213	8·496	8·710
	II	8·040	8·212	8·525	8·715

According to P. W. Bridgman, the end-terms of the Fe-Ni alloys have a different structure at room temp. for that of iron is a body-centred cube, and that of nickel, a face-centred cube. The body-centred cube persists up to between 25 and 30 per cent. of nickel, and the effect of nickel is to increase slightly the side of the fundamental cube, and slightly decrease the density. The effect is nearly linear. Beyond 25 or 30 per cent. nickel, the face-centred cube appears. The general effect of the introduction of the foreign metal is to distort the crystal structure whilst hydrostatic pressure compresses the crystal structure. With many ordinary dil. soln., the effect of adding a little solute is to compress the vol. so that the introduction of a foreign substance acts as an extra hydrostatic pressure, and the effect may be likened to that of an increase of internal pressure; with the Fe-Ni alloys the effect is just the opposite. The subject was discussed by T. D. Yensen, W. G. Burgers and co-workers, and F. Pawlek.

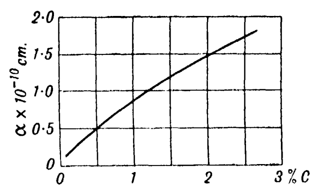


FIG. 202.—The Effect of Carbon on the Lattice Parameter of Nickel-Steels.

A. Sauveur and E. L. Reed discussed dendritic segregation in the nickel-steels. Long annealing intensifies the dendritic pattern, and quenching in brine does not remove it. The axes of the dendrites are pearlitic and the fillings are martensitic. Carbon intensifies the formation of dendrites, and the presence of phosphorus is not necessary for their formation. J. Young found that in the Widmanstätten structure of meteoric iron, the (110)-planes of the kamacite are parallel to the (111)-planes of tænite, and that the structure of plessite is the same. For Neumann's lines found in kamacite, and α-iron with their body-centred lattices, but not in tænite, and γ-iron with their face-centred lattices, *vide* the crystallization of iron. A. O. Jung made analogous observations with meteoric irons. For T. Kase's observations, *vide* the crystallization of iron. H. C. H. Carpenter and S. Tamura found that kamacite shows Neumann's bands, and infer that they are due to strain developed by the impact of the meteorite on the earth's surface. When slowly cooled from 800°, the bands and the crystals of cohenite disappear. Both tænite and plessite show a tendency to diffuse into kamacite, forming a martensitic acicular structure.

The density determinations agree with the assumption that the solid soln. consists of a simple substitution of iron and nickel atoms in the space-lattice. W. Brown found that with nickel-steels containing 5·04 per cent. manganese, 0·6 per cent. carbon, and 14·55, 19·00, and 25·00 per cent. nickel, the **specific gravities** were 7·8272, 7·8542, and 7·9101 respectively, and the sp. vols. 0·12776,

0·12732, and 0·12642 respectively. Up to 20 per cent. nickel, the addition of every 1 per cent. of nickel increases the sp. vol. by about 0·00003 c.c., so that if Ni denotes the percentage of nickel, the sp. vol. of these steels is represented by 0·1269−0·00003 Ni. Observations were made by T. D. Yensen. C. E. Guillaume found the sp. gr. of nickel-iron alloys to be:

Nickel	5·0	19·0	26·2	30·4	34·6	37·3	39·4	44·4	100 per cent.
Sp. gr.	7·787	7·913	8·096	8·049	8·066	8·005	8·076	8·120	8·750

The sp. gr. of nickel-steel is dependent on the proportion of contained nickel, and on the structure of the steel. J. Hopkinson pointed out that the transformations of 22 and 25 per cent. nickel alloys from the non-magnetizable to the magnetizable state by cooling to −100° is accompanied by such increases in vol. that the sp. gr. on return to room temp. are lowered by about 2 per cent. Thus,

	25 per cent. Ni	22 per cent. Ni
After heating (non-magnetizable)	8·15 at 15·1°	8·13 at 16·5°
After cooling (magnetizable)	7·99 at 14·5°	7·96 at 15·6°
After re-heating (non-magnetizable)	8·15 at 18·0°	8·12 at 18·2°
After again cooling (magnetizable)	7·97 at 22·0°	7·95 at 21·3°

Hence, a rod of 30 per cent. nickel-steel becomes longer not shorter when dipped in liquid air. This corresponds with the fact that the production of martensite is attended by an increase in vol. R. A. Hadfield found:

Carbon	0·19	0·13	0·19	0·17	0·23	0·16	0·14 per cent.
Nickel	0·27	0·95	3·82	7·65	15·48	24·51	28·07 ,,
Sp. gr.	7·691	7·785	7·777	7·743	7·752	7·810	8·054

H. Tomlinson observed:

Nickel	0	22	25	30	100 per cent.
Sp. gr. Hard-drawn	7·630	7·794	7·930	7·916	8·707
Sp. gr. Annealed	7·759	7·917	8·045	8·000	8·739

J. H. Andrew and H. A. Dickie, H. C. H. Carpenter and co-workers (Table XIV), F. Hegg, J. Riley, M. Rudeloff, B. Simmersbach, etc., made observations on the sp. gr. of these alloys. For sp. gr. calculated from the space-lattices, *vide supra.* W. C. Ellis and co-workers gave 8·01 for the sp. gr. of the Fe : Ni (70 : 30) alloy; also for the Fe : Ni : Cr : Mn (68 : 29 : 2 : 1) alloy. Z. Nishiyama found the sp. gr., and the elastic modulus, E kgrms. per sq. cm., at 15·4° to 15·8°, to be:

Ni	0	1	2	3	4	5 per cent.
Sp. gr.	7·8653	7·8640	7·8640	7·8558	7·8604	7·8674
$E\times10^{-6}$	2·178	2·147	2·113	2·079	2·078	2·049

A. Osawa found the results indicated above for the sp. gr. of samples of iron-nickel alloys annealed at 1150° for an hour, and also for samples immersed once in liquid air. The results for the nickel-steels are plotted in Fig. 203. The dotted line in Fig. 203 represents the assumed progress of the sp. gr. curve if no transformation of the metal occurred; and it represents the result if the sample immersed in liquid air were free from cracks. E. Houdremont and E. Bürklin studied the vol. changes due to cold-work. A. B. Everest and co-workers found that the sp. gr. of the nickel-silicon cast irons are within the limits normally given for grey and white cast irons. The sp. gr. falls fairly rapidly as silicon is increased, whereas the change caused by nickel is at first a small decrease in sp. gr. followed by a gradual increase when the proportion of nickel is large. W. Brown

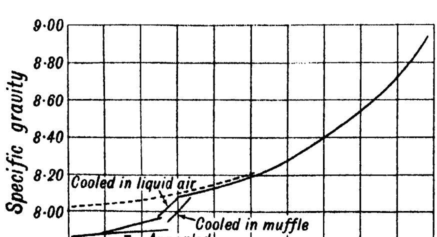


FIG. 203.—The Specific Gravity of Nickel-Steels at 18°.

detected no marked change in the specific volume of steels with up to 20 per cent. of nickel, and with more than this proportion of nickel, the sp. vol. increased 0·00033 c.c. for each per cent. of nickel. C. Benedicks and co-workers studied the effect of nickel on the sp. vol. of iron—*vide supra*, Figs. 178, **13.** 66; and the effects at 1500° and 1550° are, in general, additive, but there is a pronounced maximum with 34·5 per cent. of nickel, Fe_2Ni—invar has 36 per cent. C. Benedicks compared the maximum in the sp. vol. curve with the anomaly exhibited by water between 0° and 4°, Fig. 204. P. Chévenard observed a maximum on the sp. vol. with 35 per cent. of nickel; and G. Phragmen, a maximum with 38 per cent. of nickel. The effect of nickel on cast iron was studied by O. Bauer and H. Sieglerschmidt, L. Thiery, and P. D. Merica. P. Chévenard represented the sp. vol. as a function of the concentration in Fig. 205. He said that the curve at 0° is formed of two branches: the first branch *AB* is a straight line and represents stable alloys; the second branch *CDEF* commences with a marked anomaly corresponding with an abnormal reversible dilation. At 750°, and near −273° (obtained by extrapolation), the curves do not show this anomaly. The breaks in the curves correspond with the compounds Fe_2Ni and $FeNi_2$.

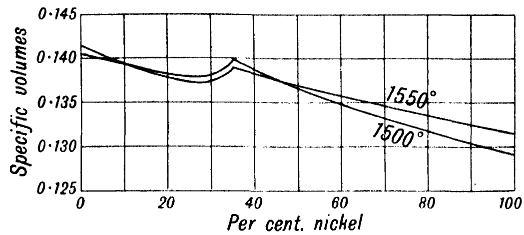


FIG. 204.—The Specific Volume Curves of Molten Nickel-Iron Alloys.

T. Kase gave the results in Table XII for the scleroscopic hardness of the nickel-iron alloys, and the corresponding microstructures.

TABLE XII.—THE HARDNESS AND MICROSTRUCTURE OF THE NICKEL-IRON ALLOYS.

Nickel (per cent.)	Microstructures		Scleroscopic hardness	
	Annealed	Quenched in liquid air	Annealed	Quenched in liquid air
0	Ferrite	Not changed	16·3	16·5
10·90	Martensite	Martensite	23·0	23·5
15·20	,,	,,	27·7	30·7
19·10	,,	,,	35·2	36·5
25·22	,,	,,	28·2	36·4
26·90	Austenite	,,	25·1	34·2
30·00	,,	,,	12·8	32·5
32·90	,,	,,	13·1	32·2
34·85	,,	Not clear	13·2	13·3
37·10	,,	Not changed	13·2	13·3
39·25	,,	,,	14·7	14·7
50·02	,,	,,	12·1	12·1
60·34	,,	,,	12·2	12·3
69·36	,,	,,	12·1	12·1

J. Riley found that the introduction of nickel increases the hardness of steel, but when 20 per cent. has been added, successive additions of nickel tend to make the steel softer and more ductile, and even to neutralize the hardening effect of carbon. The results of L. Guillet are summarized in Fig. 207. H. C. H. Carpenter and co-workers' results are indicated in Table XIV, and W. H. Hatfield's in Table XIX. For T. Kawai's observations, see Fig. 206. Observations were also made by J. H. Andrew, O. Dahl, H. A. Dickie, S. F. Dorey, O. Forsman, L. E. Gilmore, J. N. Greenwood, K. V. Grigoroff, L. Guillet, L. Guillet and M. Ballay, W. J. de Haas and R. Hadfield, W. Hanby, D. Hanson, L. Jannini, H. Jungbluth, T. Kase,

G. H. Keulegan and M. R. Houseman, J. B. Kommers, A. Kussmann and B. Scharnoff, G. V. Luerssen and O. V. Greene, T. Mezaki, A. Osawa, C. Pfannenschmidt, F. Rapatz and H. Pollack, G. A. Roush, K. Sasakawa, F. Sauerwald and K. Knehans, H. Schottky, G. Tammann and V. Caglioti, K. Taniguchi, and H. Unger. A. B. Everest and co-workers showed that the hardness curves of nickel-silicon cast irons correspond with the microstructures. There is a softening through graphitization, and a hardening through the sorbite and martensite ranges, and finally softening through the austenitic conditions. Thus, chilling softens the

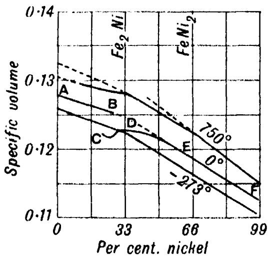


FIG. 205.—Specific Volumes of Nickel-Steel.

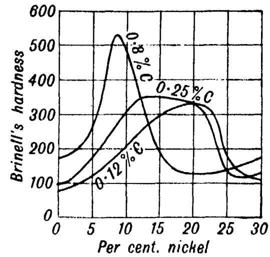


FIG. 206.—Brinell's Hardness of Nickel-Steel.

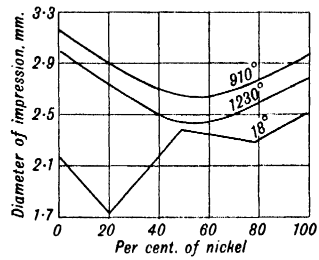
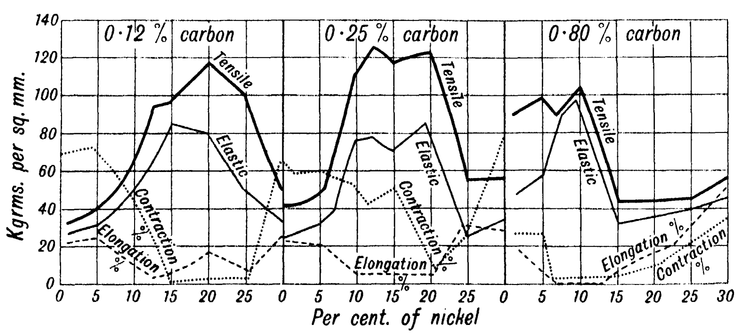


FIG. 207.—The Hardness of Iron-Nickel Alloys.

alloys towards the end of the martensitic range. L. Guillet and J. Cournot studied the effect of temp. between 20° and —190° on the hardness and resilience. For F. Robin's observations, *vide* Fig. 206. E. Kothny showed that the effect of annealing at different temp. on the hardness of a steel with 0·14 per cent. of carbon, 0·68 per cent. of manganese, and 4·75 per cent. of nickel was 159·6 when unannealed, and when annealed at:

	650°	680°	710°	720°	740°	780°	830°	850°
Hardness .	179·1	193·5	177·9	164·8	157·5	150·5	151·7	149·9

F. Sauerwald measured the hardness of the alloys at different temp. in terms of the diameter in mm. of the impression made by a ball of 1·256 kgrms. falling 14 cms. At 18°, the results are complicated by the presence of more than one constituent. A. L. Kimball studied the internal friction of nickel-steels.



FIGS. 208, 209, 210.—The Mechanical Properties of Nickel Steels.

R. Knittel studied the effect of nickel on the wearing of iron. For T. Kawai's observations on the effect of cold-work, see Fig. 216. L. Guillet, Figs. 208 to 210, found that, other things being equal, the **mechanical properties** of pearlitic nickel-steels show a high elastic limit the higher the proportion of nickel without the values exceeding by more than 10 to 20 kgrms. those obtained with ordinary steels having the same percentage of carbon. The elongation, reduction in area, and resistance to shock are in no way diminished by the presence of nickel. The hardness is slightly increased. The martensitic steels

have a high tensile strength, a very high elastic limit, and a low elongation. They are brittle, and very hard. The maximum tensile strength is obtained with a low proportion of carbon—0·20 to 0·30 per cent. This is attributed to the restricted area of martensite in steels with a high proportion of carbon, for in such steels, the martensite is usually plentifully admixed with γ-iron or ferrite. With over 0·50 per cent. of carbon, the martensite usually consists of large needles readily coloured by picric acid like the so-called troosto-sorbite. The polyhedral steels containing γ-iron are characterized by a medium tensile strength, low elastic limit, very high elongation, and reduction in area. They have a high resistance to shock and medium hardness.

Observations on the mechanical properties were made by A. Abraham, O. Bauer and E. Piwowarsky, G. D. Bengough, H. Brearley, M. Brocard, G. Brodsky, D. H. Browne and H. J. Porter, G. K. Burgess, A. Campion, H. Carrington, C. Caspar, P. Chévenard, G. H. Clamer, A. L. Colby, G. Colonnetti, M. Combe, E. F. Cone, F. B. Coyle, J. A. Coyle, F. Dagner, S. J. E. Dangerfield and co-workers, T. G. Digges, J. Devis, E. Dixon, J. W. Donaldson, V. Ehmcke, F. A. Fahrenwald, H. J. French and co-workers, T. Fujiwara, G. Gabriel, R. Gaillard, E. H. S. Gallik, J. Garnier, F. L. Garrison, N. J. Gebert, R. C. Good, E. Greulich, L. Guillet and co-workers, D. Hanson, T. Harrington, W. Haufe, C. C. Hodgson, W. A. Johnson, J. J. A. Jones, L. Katona, M. Kersten, G. Klein, K. R. Koch and C. Dannecker, H. Koppenberg, V. N. Krivobok, F. Kupelwieser, W. Liestmann and C. Salzmann, C. C. Longridge, T. D. Lynch and co-workers, F. J. McGrail, H. P. McIntosh, C. McKnight, R. S. MacPherran, E. Marcotte, P. Marsich, J. A. Mathews, E. Mercadier, P. D. Merica and R. G. Waltenberg, L. S. Moisseiff, P. Moulan, K. Nagasawa, J. Negru, A. L. Norbury, B. Palmgren, S. W. Parker, N. B. Pilling and T. E. Kihlgren, E. Piwowarsky and H. Nipper, E. Piwowarsky and co-workers, H. J. F. Porter, A. M. Portevin, A. M. Portevin and P. Chévenard, F. Renaud, J. Riley, F. Robin, W. Rohn, W. Rosenhain and co-workers, A. Rys, K. Sasakawa, F. Sauerwald and co-workers, H. Sawamura, A. Schulze, F. T. Sisco, O. Smalley, E. K. Smith and H. C. Aufderhaar, S. C. Spalding, H. Steudel, B. Stoughton and W. E. Harvey, Y. Taji, A. N. Talbot and H. F. Moore, K. Taniguchi, J. J. Thomas and J. H. Nead, J. Trantim, T. Turner, O. Vogel, S. I. Volfson, A. J. Waddell, W. H. Warren, G. B. Waterhouse, J. F. Webb, H. Wedding, T. H. Wickenden and J. S. Vanck, T. J. Wood, and A. G. Zima.

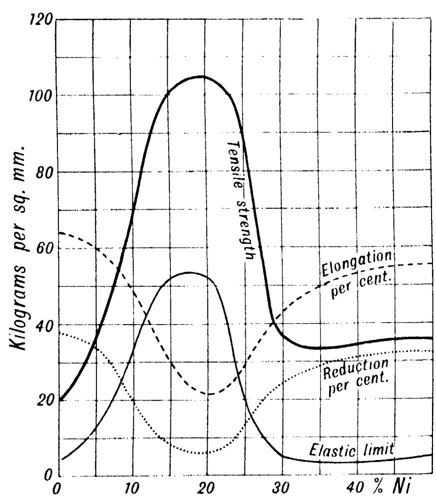


FIG. 211.—Mechanical Properties of Nickel-Steel (0·2 per cent. carbon).

A. L. Kimball and D. E. Lovell gave 21×10^{11} dynes per sq. cm. for the elastic modulus of swaged 3 per cent. nickel-steel; and $1{\cdot}10\times10^{15}$ for the internal friction. The results of A. Dumas, R. A. Hadfield, M. Rudeloff, and the Fonderies, Forges et Aciérs de Saint-Etienne are summarized in Fig. 211, for steels with about 0·20 per cent. of carbon. Expressing the results for the tensile strength and elastic limit in kgrms. per sq. mm.:

Nickel (per cent.)	Carbon (per cent.)	Tensile strength	Elastic limit	Elongation (per cent.)	Reduction of area (per cent.
29 (L. Dumas) .	0·11	52	34	34·0	64·0
	0·32	68	45	33·0	57·0
30 (L. Guillet) .	0·12	45	29	29·5	63·9
	0·25	56	33	32·0	71·3
	0·80	80	48	32·5	50·0
35 (W. Giesen) .	0·15	50	42	35·5	71·8
	0·30	81	48	38·3	78·6
	0·95	79	61	39·1	62·7

Z. Nishiyama's results for the elastic modulus are indicated above. While L. Guillet said that the properties are almost independent of the proportion of

carbon, W. Giesen observed that this is not always the case. His results are shown in Table XIII. He concluded that nickel-steels with 0 to 12 per cent. of

TABLE XIII.—MECHANICAL PROPERTIES OF NICKEL-STEELS.

Nickel (per cent.)	Tensile strength (lbs. per sq. in.)			Elastic limit (lbs. per sq. in.)		
	0·15 per cent. C	0·3 per cent. C	0·95 per cent. C	0·15 per cent. C	0·3 per cent. C	0·95 per cent. C
2·5	55,042	50,162	130,565	45,939	58,456	68,695
5·0	74,812	163,704	165,990	64,857	127,578	142,754
10·0	99,701	178,211	168,255	85,763	128,574	102,120
15·0	144,076	146,210	134,264	114,351	98,563	126,125
20·0	175,794	142,086	130,423	153,028	137,108	128,431
25·0	186,978	198,834	187,314	139,097	130,565	141,801
30·0	146,641	122,742	125,730	99,985	78,651	89,319
35·0	71,540	115,774	112,786	59,167	68,980	87,470

Nickel (per cent.)	Elongation (per cent.)			Reduction of area (per cent.)		
	0·15 per cent. C	0·3 per cent. C	0·95 per cent. C	0·15 per cent. C	0·3 per cent. C	0·95 per cent. C
2·5	26·0	24·0	22·0	81·4	71·3	65·2
5·0	12·0	8·0	8·7	30·2	28·7	22·3
10·0	10·0	4·6	9·1	59·2	37·6	31·6
15·0	0·9	9·1	12·3	2·1	41·3	38·4
20·0	17·0	11·6	19·1	6·2	9·7	11·4
25·0	21·0	6·7	7·8	4·3	4·3	3·9
30·0	9·0	32·1	38·6	5·1	32·5	29·8
35·0	35·5	38·3	39·1	71·8	78·6	62·7

nickel and 0·3 per cent. of carbon, and those with 0 to 7 per cent. of nickel and 0·95 per cent. of carbon, with a pearlitic structure, differ very little from ordinary carbon steels with the same carbon content in respect of tensile strength, ductility, yield-point, elongation, hardness, and brittleness. On the other hand, with steels having the martensitic structure, the limits of stretching and breaking strain are very high if, on the one hand, with 0·3 per cent. carbon, the nickel content does not exceed 12 to 30 per cent., and, on the other hand, with 0·95 per cent. carbon, the nickel content lies between 0·6 and 18 per cent. The ductility and brittleness are here very low, whilst the hardness is extremely high. With the γ-iron structure, the ductility is remarkably high provided the nickel content, in the presence of 0·95 per cent. carbon, exceeds 18 per cent., the same also applying to cases where, with a low carbon content (about 0·3 per cent.), the nickel content exceeds 30 per cent. In both instances, however, the elastic limit and the brittleness are low, and the breaking strength medium ; whilst, in respect of hardness, highly divergent results were obtained, so that it was impossible to establish any definite standards. One remarkable point is that the martensitic nickel-steels of divergent carbon and nickel content do not attain their maximum breaking strength and elastic limit with the highest carbon content. K. Yuasa found that with a very sensitive apparatus, nickel-steel under tension and torsion, between room temp. and 349°, exhibited a number of sudden yieldings in steps as it began to fail—*vide* iron.

M. Rudeloff found for various stresses in kgrms. per sq. mm. :

Nickel . . .	0·05	7·84	15·59	29·77	59·6	98·39 per cent.
Limit proportionality	6·0	22·8	16·0	6·3	6·0	3·6
Yield-point . .	14·6	44·2	—	12·5	12·5	9·1
Breaking strength .	32·4	56·2	41·0	9·9	37·8	30·5
Modulus of elasticity .	22,525	19,280	16,200	12,300	14,490	16,870
Resistance to shearing	26·6	43·5	67·7	35·4	37·9	34·7

A. M. Portevin studied the resistance to shearing, and the tensile strength of the nickel-steels. For C. L. Clark and A. E. White's observations on the proportional limit of steel with 0·10 per cent. of carbon, and 4·95 of nickel, *vide* Fig. 276 in connection with the nickel-chromium steels. The results of H. C. H. Carpenter and co-workers for nickel-steels with 0·40 to 0·52 per cent. of carbon and 0·75 to 1·03 per cent. of manganese, are summarized in Table XIV. The steels were forged, and cooled from 800°. Observations were reported by R. Baumann,

TABLE XIV.—MECHANICAL PROPERTIES OF NICKEL-STEELS.

Nickel (per cent.)	Bending test	Tensile tests (tons per sq. in.)					Torsion tests	
		Yield-point	Max. stress	Elastic ratio	Elongation (per cent.)	Reduction of area (per cent.)	Twisting moment (inch-lbs.)	Angle of twist at fracture
0	180°	21·00	38·19	0·55	25·0	51·73	4·277	—
1·20	180°	23·93	40·93	0·58	21·0	42·80	5·077	405°
2·15	180°	23·67	41·52	0·57	24·5	51·83	5·609	621°
4·25	180°	29·16	47·86	0·61	20·0	33·06	5·071	468°
4·95	30°	33·95	60·09	0·56	2·0	3·71	6·429	177°
6·42	10°	None	110·57	—	nil	nil	7·497	42·6°
7·95	5°	None	77·38	—	nil	nil	7·938	20·1°
12·22	10°	34·56	80·24	0·43	1·0	1·63	8·621	31·5°
15·98	60°	28·53	80·24	0·35	5·5	7·33	7·329	118·5°
19·91	180°	15·33	43·92	0·35	55·0	63·11	5·662	690°

Nickel (per cent.)	Shock tests			Hardness tests			Sp. gr. at 17° to 18°	Sp. vol. at 17° to 18°
				Indentation in 0·001 in.				
	Fall of 46·7 lbs. hammer (in.)	Energy absorbed (inch-lbs.)	Bending angle	Load 1·5 tons	Load 2·5 tons	Brinell's hardness		
0	13·23	451	18·0°	7·2	15·0	202	7·880	0·1269
1·20	13·05	428	17·0°	6·4	14·5	207	7·890	0·1267
2·15	13·67	454	16·5°	7·0	19·5	212	7·884	0·1268
4·25	13·92	460	15·5°	6·0	12·3	217	7·867	0·1271
4·95	13·67	217	broken	4·2	8·7	321	7·876	0·1270
6·42	13·67	105	broken	2·5	5·5	532	7·885	0·1268
7·95	14·15	230	broken	2·5	5·7	578	7·883	0·1269
12·22	14·17	436	7·5°	3·2	6·2	555	7·904	0·1265
15·98	13·33	432	14·5°	5·0	10·3	293	8·026	0·1246
19·91	13·77	452	28·0°	16·0	40·0	131	8·122	0·1231

W. Beardmore, P. Blum, D. H. Browne, M. Brocard, H. H. Campbell, F. L. Coonan, H. A. Dickie, F. A. Fahrenwald, J. Galibourg, E. Heller, O. von Keil and F. Ebert, E. Kothny, W. Kurose, F. C. Langenberg, J. List, C. McKnight, J. V. Murray, I. Musatti and G. Calbiani, P. Oberhoffer and E. Piwowarsky, E. Piwowarsky and co-workers, R. S. Poister, H. J. Porter, E. Preuss, F. Renaud, M. Rudeloff, H. Souther, G. Surr, L. Thiery, J. J. Thomas and J. H. Nead, M. Vasuari, A. J. Waddell, W. H. Warren and S. H. Barraclough, G. Wassermann, and R. H. Watson. H. Tomlinson found for Young's modulus, and the rigidity in grams per sq. cm. $\times 10^6$, and for the logarithmic decrement (base 10):

Nickel		0	22	25	30	100 per cent.
Young's modulus	Hard-drawn	1862	1590	1590	1428	2271×10^6
	Annealed .	1981	1626	1555	1328	2175×10^6
Rigidity	Hard-drawn	704	529	547	527	723×10^6
	Annealed .	704	596	547	527	723×10^6
Logarithmic decrement	Hard-drawn	0·001214	0·000809	0·000674	0·000762	0·002005
	Annealed .	0·000914	0·000441	0·000212	0·000595	0·000852

R. W. Moffatt found that nickel-steel castings, normalized and reheated, have a high resistance to impact at a low temp.

The temper brittleness of the nickel-steels was examined by F. Rogers; and the effect of the initial temp. on the physical properties, *vide* the physical properties of iron, **66**. 13, 18. F. Robin found that the resistance of pearlitic nickel-steels to crushing is similar to that of pearlitic carbon steels (*q.v.*); possibly the maximum in the curve is slightly deflected towards increasing temp. Above 800°, the curves are almost linear, and their resistance increases slowly. The resistance to crushing of martensitic nickel-steels increases rapidly with temp. Austenitic nickel-steels, and steels with a high proportion of nickel, have a resistance which decreases uniformly and slowly up to 600°, and their curvature, at this temp., is rectilinear, particularly where the percentage of nickel is high. From 600° upwards, the resistance diminishes rapidly; at 700°, the value of the resistance to crushing is similar with all the steels, and the curves resemble one another.

J. Hopkinson found that by the intense cooling of the steel with about 25 per cent. of nickel the tensile strength, at room temp., was raised from 50 tons per sq. in. and 32 per cent. elongation to 87 tons per sq. in. and 7·5 per cent. elongation. C. E. Guillaume showed that the anomalies observed in the dilation of nickel-steels with variations of temp. in the zone of the transformations, are also shown by the coeff. of elasticity. This is illustrated by Fig. 212 for reversible and irreversible

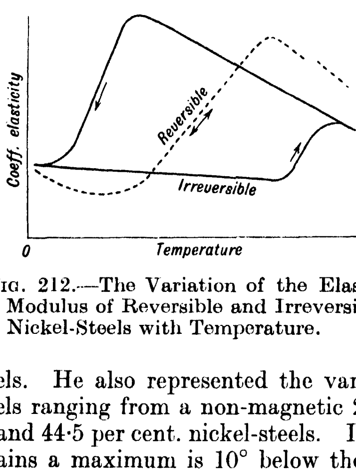


FIG. 212.—The Variation of the Elastic Modulus of Reversible and Irreversible Nickel-Steels with Temperature.

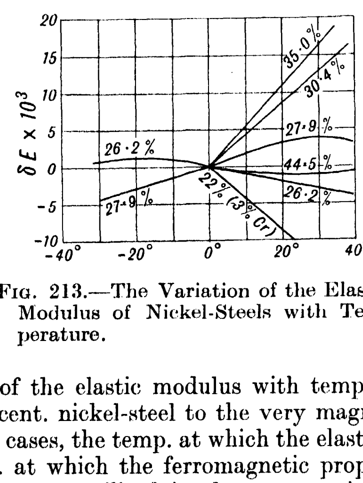


FIG. 213.—The Variation of the Elastic Modulus of Nickel-Steels with Temperature.

steels. He also represented the variation of the elastic modulus with temp. for steels ranging from a non-magnetic 22 per cent. nickel-steel to the very magnetic 36 and 44·5 per cent. nickel-steels. In these cases, the temp. at which the elasticity attains a maximum is 10° below the temp. at which the ferromagnetic property appears when the steel is cooled. The facts are utilized in the construction of precision chronometers. The modulus of elasticity, E, in metric tons per sq. mm., were found by C. E. Guillaume to be:

Ni .	5·0	15·0	26·2	31·4	35·2	37·2	39·4	44·3	70·0	100 per cent.
E .	21·7	19·1	18·5	15·5	14·9	14·6	15·1	16·3	19·8	21·6

and for

Ni . .	12·2	16·2	16·8	34·8	35·7	36·4 per cent.
Cr . .	1·0	2·5	1·0	1·5	1·7	0·9 ,,
E . .	19·0	19·6	18·3	15·5	15·7	15·7

while he gave for the change in the elastic modulus with temp., for a non-magnetic alloy with 22·0 per cent. of nickel and 3·0 per cent. of chromium, $19·67(1-394\times10^{-6}\theta)$; for, say, a slightly magnetic alloy with 26·2 per cent. of nickel, $18·54\{1-(51·6\theta+95\theta^2)10^{-6}\}$; for a slightly magnetic alloy with 27·6 per cent. of nickel, $18·06\{1+(1040-1·72\theta^2)10^{-6}\}$; for a magnetic alloy with 30·4 per cent. of nickel, $15·96(1+389\times10^{-6}\theta)$; for a very magnetic alloy with 35 per cent. of nickel

15·04(1+464×10⁻⁶θ); and for a very magnetic alloy with 44·5 per cent. of nickel, $16\cdot40\{1-(43\cdot6\theta-0\cdot62\theta^2)10^{-6}\}$. H. Fay and J. M. Bierer found that with nickel-steels approximating 3·5 per cent. of nickel, and 0·35 per cent. of carbon, oil-quenching followed by a 2 hrs.' tempering gave higher values for the tenacity and ductility than air-cooled or furnace-cooled specimens. They said that the most suitable temp. for quenching nickel-steels is between 800° and 850°, and that with higher temp. the structure becomes coarser. E. Heyn and O. Bauer noticed that nickel-steel is apt to split with an excessive forging heat, and that the most favourable temp. depends on the dimensions of the piece, and the length of the heating period. A. McWilliam and E. J. Barnes studied the heat treatment of steels with about 3 per cent. of nickel, and 0·06 to 0·91 per cent. of carbon. H. Meyer, and E. F. Cone studied the effect of heat treatment on some nickel-steels; E. Kothny found that with a steel containing 0·14 per cent. carbon, 0·68 manganese, and 4·75 nickel, and then annealed at different temp. (kgrms. per sq. mm.):

Annealing	none	650°	680°	710°	720°	740°	780°	830°	
Stretching limit	38·9	32·7	28·6	34·3	34·4	37·2	37·1	36·2	
Tensile strength	33·8	63·3	66·5	59·8	57·9	54·2	52·1	51·9	
Elongation	24·7	16·9	20·8	21·1	25·1	24·7	26·5	27·3	per cent.
Reduction area	64·7	50·6	55·7	66·7	67·6	66·2	65·2	65·4	,,

C. L. Clark and A. E. White measured the tensile properties of nickel-steels at elevated temp. C. E. Guillaume found for the elastic modulus, E, of nickel-iron alloys:

Nickel	5·0	19·0	26·2	27·9	30·4	37·3	39·4	70·3	100 per cent.
$E\times10^{-6}$	2·17	1·77	1·85	1·81	1·60	1·40	1·51	1·98	2·16

K. Honda and T. Terada gave for the elasticity, E, of nickel-steels with 28·74 per cent. of nickel, $1\cdot570\times10^{12}$ with a load of 1480 grms. per sq. mm., and $1\cdot702\times10^{12}$ with a load of 9710 grms. per sq. mm.; with 50·72 per cent. nickel, $1\cdot376\times10^{12}$ with a load of 1780 grms. per sq. mm., and $1\cdot619\times10^{12}$ with a load of 11,650 lbs. per sq. in.; and with 70·32 per cent. nickel, $1\cdot866\times10^{12}$ with a load of 1500 grms. per sq. mm., and $1\cdot996\times10^{12}$ with a load of 7030 grms. per sq. in. The coeff. of rigidity of steels with 28·74, 50·72, and 70·30 per cent. nickel were respectively $0\cdot613\times10^{-12}$, $0\cdot365\times10^{-12}$, and $0\cdot640\times10^{-2}$. R. A. Hadfield found that nickel helps to counteract the brittleness which iron develops when it is cooled to low temp., say −182°. E. L. Hancock found that when stressed to its ultimate limit, but not fractured, nickel-steel will recover so as to show a higher ultimate strength and a higher limit of elasticity, and that carbon steels recover more quickly than nickel-steels. For T. Kawai's results on the impact test, *vide* the impact test for iron, Figs. 212 to 214—**13**. 66, 18. The effect of nickel in cast iron, studied by J. S. Vanick, L. Guillet, O. Bornhofen and E. Piwowarsky, T. Meierling, F. Roll, A. B. Everest, P. D. Merica, etc., has been discussed in connection with cast iron.

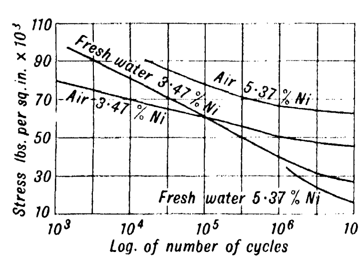


FIG. 214.—The Fatigue and Corrosion-Fatigue Tests of Nickel-Steels.

D. J. McAdam, and T. S. Fuller observed that the simultaneous action of corrosion and fatigue—corrosion-fatigue—causes failure at stresses far below the ordinary endurance limit—*vide* the corrosion of iron. According to D. J. McAdam, the results of tests of nickel-steel simultaneously exposed to the action of fatigue and corrosion in air (fatigue test), and to the action of fresh, carbonate water (corrosion-fatigue test) using stresses alternating 1450 revs. per minute, are indicated in Fig. 214. The graph shows the relation

between the stress and the logarithm of the number of cycles for failure. The static, fatigue, and corrosion-fatigue tests are:

	3·47 per cent. Ni		5·37 per cent. Ni	
	Annealed	Quenched	Annealed	Quenched
Tensile strength .	92,500	124,800	121,800	132,700 lbs. per sq. in.
Total elongation .	29·9	21·6	18·0	18·7 per cent. in 2 ins.
Reduction of area .	58·5	65·8	25·8	40·5 per cent.
Endurance limit .	49,000	69,000	55,000	66,000 lbs. per sq. in.
Corrosion-fatigue .	29,000	25,000	21,000	19,000 ,, ,,

R. F. Mehl and B. J. Mair gave $0{\cdot}0_685$ for the **compressibility** coeff. of invar, and found the result much higher than the value calculated by the mixture rule for α-iron, they therefore used the coeff. for nickel, and calculated the value for the compressibility of γ-iron, which exceeds the value for α-iron.

F. Robin studied the **acoustic properties** of the nickel-iron alloys with a high proportion of nickel, which have resonance curves peculiar to themselves; the duration of the sound, with variations of temp., after having gradually increased, falls very rapidly just before the complete disappearance of the magnetism. The resonance at normal temp. falls and then rises again when the percentage of nickel is increased, the sinuosity of the curve becomes less, until it disappears when about 5·8 per cent. of nickel is present, and does not reappear again in the case of pure nickel until a temp. of 300° is attained.

M. Rudeloff found that the coeff. of **thermal expansion** decreased as the proportion of nickel increased up to 16 per cent., but was greater with 98 per cent. nickel than with iron alone. Thus, with no nickel, the expansion for 1° in micromillimetres per metre was $11{\cdot}56+0{\cdot}0056\theta$; with 4 per cent. nickel, $10{\cdot}90+0{\cdot}0056\theta$; and with 16 per cent. nickel, $10{\cdot}30+0{\cdot}0056\theta$.

C. E. Guillaume observed that the mean coeff. of linear expansion of nickel-iron alloys between 0° and 38°, taking the value for iron alone to be $10{\cdot}354+0{\cdot}00053\theta$, was for 5·0 per cent. nickel, $10{\cdot}529+0{\cdot}003626\theta$; for 26·2 per cent., $13{\cdot}103+0{\cdot}021236\theta$; for 28·7 per cent., $10{\cdot}387+0{\cdot}030046\theta$; for 34·63 per cent., $1{\cdot}373+0{\cdot}0025\theta$; for 35·6 per cent., $0{\cdot}877+0{\cdot}001276\theta$; for 37·3 per cent., $3{\cdot}457-0{\cdot}006476\theta$; for 43·6 per cent., $7{\cdot}992-0{\cdot}002736\theta$; for 48·7 per cent., $9{\cdot}901-0{\cdot}000676\theta$; for 50·7 per cent., $9{\cdot}824+0{\cdot}002436\theta$; for 70·3 per cent., $11{\cdot}890+0{\cdot}003876\theta$; and for 100 per cent., $12{\cdot}661+0{\cdot}005506\theta$. The mean coeff. for 12·2 per cent. Ni with 1 per cent. Cr is represented by $11{\cdot}714+0{\cdot}005086\theta$; for 16·7 Ni, and 1 Cr, by $11{\cdot}436+0{\cdot}001706\theta$; for 16·2 Ni, and 2·5 Cr, by $19{\cdot}496+0{\cdot}004326\theta$; for 21·3 Ni, and 3 Cr, by $18{\cdot}180+0{\cdot}004266\theta$; by 34·8 Ni, and 1·5 Cr, by $3{\cdot}580+0{\cdot}001326\theta$; with 35·7 Ni, and 1·7 Cr, by $3{\cdot}373+0{\cdot}001656\theta$; and for 36·4 Ni+0·9 Cr, by $4{\cdot}433-0{\cdot}003926\theta$. The true coeff. of linear expansion $\alpha\times10^6$, at $\theta°$ for a 30·4 per cent. Ni alloy is $4{\cdot}570+0{\cdot}0235\,(\theta-0)$ between 0° and 110°; $7{\cdot}15+0{\cdot}104\,(\theta-110)$ between 110° and 164°; and $12{\cdot}60+0{\cdot}008\,(\theta-164)$ between 164° and 220°; for 31·4 per cent. nickel alloy, $\alpha\times10^6=3{\cdot}395+0{\cdot}0150\,(\theta-0)$ between 0° and 122°; $5{\cdot}25+0{\cdot}128\,(\theta-122)$ between 122° and 182°; $13{\cdot}00+0{\cdot}036\,(\theta-182)$ between 182° and 220°; for a 34·6 per cent. nickel alloy, $\alpha\times10^6=1{\cdot}373+0{\cdot}0047\,(\theta-0)$ between 0° and 142°; and $2{\cdot}05+0{\cdot}065\,(\theta-142)$ between 142° and 220°; and for a 37·3 per cent. nickel alloy, $\alpha\times10^6=3{\cdot}457+0{\cdot}0072\,(\theta-0)$ between 0° and 150°; and $2{\cdot}37+0{\cdot}011\,(\theta-150)$ between 150° and 220°.

G. Charpy and L. Grenet obtained the values indicated in Table XV for the mean coeff. of thermal expansion, $\alpha\times10^6$, for the stable form of nickel-steels. The numbers in brackets indicate the temp. at which a transformation begins. H. C. H. Carpenter and co-workers gave for the coeff. of expansion, α, of the nickel-steels indicated in Table XIV:

Nickel .	1·20	2·15	4·25	4·95	6·42	7·95	12·22	15·98	19·91 per cent.
$\alpha\times10^6$.	11·22	11·12	11·36	12·07	12·23	12·13	13·28	17·54	19·65

Observations were also made by C. Benedicks and P. Sederholm, E. A. Blomqvist, J. Carnera, W. M. Cohn, H. Donaldson, F. A. Fahrenwald, D. Hanson, H. Hiemenz, K. Honda and co-workers, P. C. Jones, H. Jungbluth, G. W. C. Kaye, M. Leman and co-workers, J. Mascart, H. Masumoto and S. Nara, E. Maurer and W. Schmidt, A. Merz, W. Rohn, T. F. Russell, J. W. Sands, K. Scheel, A. Schulze, F. J. Scrase, H. Sieglerschmidt, W. Souder and P. Hidnert, T. Sutoki,

TABLE XV.—THE COEFFICIENTS OF THERMAL EXPANSION OF NICKEL-STEELS.

Percentage composition of steel			Coeff. of expansion $\alpha \times 10^6$						
			Stable when cold			Stable when hot			
Ni	C	Mn	0°–200°	200°–400°	400°–600°	0°–200°	200°–400°	400°–600°	600°–900°
0	0·22	0·48	12	15	15	—	—	—	—
2·01	0·21	0·41	11	14	15	—	—	—	23
8·47	0·25	0·41	14	14	10	—	—	16	21
10·40	0·20	0·41	11·5	11	12	—	—	20	22·5
21·00	0·36	0·36	10	10	(545°)	—	17	20	20
26·90	0·35	0·36	7·8	10·5	(495°)	16·2	20	18·6	22·1
29·00	0·35	0·34	12·9	11	—	12·5	17·5	19	18·5
31·35	0·36	0·37	—	—	—	6·5	15	17	18·3
34·75	0·36	0·36	—	—	—	3·5	13·5	17	17·5
36·05	0·39	0·36	—	—	—	1·0	6·2	17·5	19
22·8	0·29	0·73	8·5	9	10	22	20	17	20
32·8	0·29	0·66	—	—	—	11	17·5	20·5	20
35·8	0·31	0·69	—	—	—	2·5	12·5	18	19
37·4	0·30	0·69	—	—	—	2·5	8·5	19	17
19·9	0·70	0·48	9	9	(560°)	23	20	18·5	29
24·6	0·78	0·45	—	—	—	16	20	19	30
25·0	0·84	0·48	—	—	—	15	19	20	28
28·8	0·78	0·48	—	—	—	10·5	18	19	26
34·3	0·70	0·45	—	—	—	2·5	13·5	17	25
34·8	0·63	0·49	—	—	—	2·5	10	18	23
20·75	0·72	0·80	13	16	(560°)	22	20	20	28
26·20	0·71	0·90	—	—	—	15	20	20	29
29·40	0·73	0·90	—	—	—	16	19	20	27
34·45	0·77	0·90	—	—	—	3	15	16	24
35·35	0·71	0·89	—	—	—	23	13	16	24
20·90	0·97	0·48	12	17	(550°)	—	20	27	27
29·90	0·89	0·43	—	—	—	12	19	18	28
21·25	0·92	0·97	—	—	—	—	15	18	32
25·40	1·01	0·79	—	—	—	15	20	20	32
29·45	0·99	0·89	—	—	—	11	19	20	29
34·50	0·97	0·84	—	—	—	3	13	18	25

S. Valentiner and J. Wallot, and A. Werner. The results of K. Honda and co-workers are represented by the continuous line in Fig. 215 ; those of A. Schulze, by the broken line ; and those of R. Vogel, by the dotted line. Observations were also made by P. Chévenard, H. Scott, C. Benedicks and P. Sederholm, H. Masumoto, and P. Hidnert and H. S. Krider. K. Honda and co-workers found that there is a minimum for about 18 per cent. of nickel ; and all found a minimum. There is a maximum with 25 per cent. of nickel for α=0·0₅16, and 36·5 per cent. of nickel.

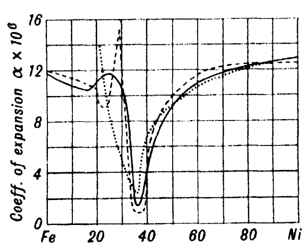


FIG. 215.—Coefficients of Thermal Expansion of Nickel-Iron Alloys.

According to C. E. Guillaume, when an irreversible nickel-steel assumes the ferromagnetic state on cooling, it undergoes an irreversible change in volume corresponding closely with the magnetic anomalies described below. The behaviour of a 15 per cent. nickel-steel, cooling from a cherry-red heat, is illustrated by Fig. 216. The vol. contraction is represented by the line AB, at B, near 130°, a rapid expansion occurs which soon attains 40μ per metre per degree. If the bar be then reheated, it does not contract according to the curve it followed on cooling, but it expands along some other line, say DC. On cooling, the bar returns to D, and then expands along the

curve *DE*. At a low temp., under the correct conditions, the contraction along the line *CD* might continue, say 15°, beyond the curve *BE*, and then the bar may be suddenly brought to the same length it would have attained at the existing temp. if it had followed the curve *BE* immediately after reaching *D*. This phenomenon is analogous to the undercooling of a saturated soln. or of a molten solid. By appropriate cooling the changes in length with temp. can be made to follow any such line, *CD*, and consequently the coeff. of expansion which is proportional to the slope of the curve, may assume with the self-same bar, any desired value in accord with the limits—10 to 20 millionths—allowed by

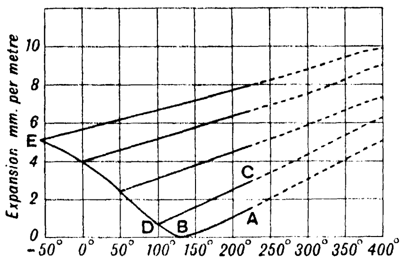


FIG. 216.—Changes in Length with Temperature of an Irreversible Nickel-Steel.

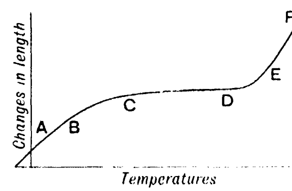


FIG. 217.—Changes in Length with Temperature of a Reversible Nickel-Steel.

the transformation. In the case of 15 per cent. nickel-steel cooling to $-60°$ is not sufficient to complete the transformation into the state which is stable at very low temp. These results agree with the observations of G. Charpy and L. Grenet, Table XV. The different irreversible steels have the same general behaviour, but show differences in the magnitude of the changes, and in the region of temp. in which the transformations occur.

Reversible steels behave differently. C. E. Guillaume represented the phenomena with reversible steels by Fig. 217. As the alloy cools from a high temp., it contracts linearly along a straight line *FE*, Fig. 217. The slope of this line corresponds with a coeff. of expansion which is greater than that of iron, or of a mixture of iron and nickel at ordinary temp., and it is reduced by increasing the proportion of nickel, except for the smaller proportions of nickel. Within the range of temp. characterized by the appearance of magnetic properties, the cooling curve changes rapidly along *ED*, and this is followed by a regular region *DC* of very small slope. At still lower temp., there is another region of rapid change, *CB*, and this is followed by a region of regular change, *BA*; the slope of the curve then corresponds with the coeff. of expansion of a mixture of iron and nickel at ordinary temp. At ordinary temp., the expansion of a 25 per cent. nickel alloy would be represented roughly by *EF*; that of a 27 to 32 per cent. nickel alloy, by *DE*; of a 36 to 37 per cent. nickel alloy, by *CD*; of a 37 per cent. alloy, by *BC*; and above this, especially above 60 per cent., by *AB*, or the portion below *A*. At high temp., each region corresponds with alloys containing greater proportions of nickel. The complete curve from *A* to *F* gradually deforms, and shifts as a whole, parallel to the axis of temp. This behaviour resembles that followed by the curve of the magnetic transformations of these alloys.

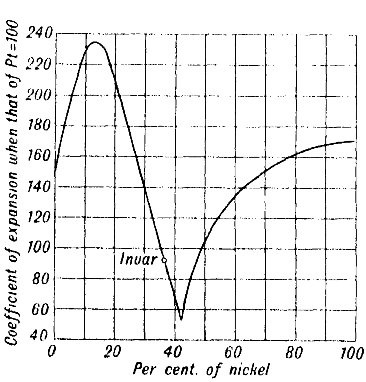


FIG. 218.—The Relative Coefficients of Thermal Expansion of the Iron-Nickel Alloys when that of Pt = 100.

C. G. Fink and C. M. De Groly gave the curve shown in Fig. 218 for the coeff. of

thermal expansion of the iron-nickel alloys between 25° and 400°, when the coefficient of expansion of platinum is 100.

A. Schulze gave the results for the coeff. of thermal expansion of the iron-nickel alloys. C. E. Guillaume's observations, indicated above, show how the thermal expansion of the alloys changes with composition. These alloys were cooled in air after a simple hot forging, and they contain the usual proportions of manganese, carbon, and silicon—in all, about 1 per cent.—*vide infra*, Fig. 220. C. E. Guillaume said that the presence of a little manganese is required to make the alloys workable; but, by keeping the proportion as small as practicable, and employing suitable thermal and mechanical treatments, it is possible to make the coeff. of thermal expansion zero, and even negative. The line *FN*, Fig. 219, connects the coeff. of expansion of iron with that of nickel at 20°, and it represents the results which would obtain if the law of mixtures was applicable. Fig. 220 shows the effects of additions of 1 per cent. of chromium or manganese on the thermal expansion. The need for a minimum proportion of manganese to render the alloy workable was also noted by A. Dumas, and P. Chévenard. By taking the necessary precautions, C. E. Guillaume obtained a mean coeff. of linear expansion, α, between zero and $\theta°$ with a negative value $\alpha \times 10^6 = -0{\cdot}552 + 0{\cdot}003776\theta$; and by adjusting the conditions to secure only part of the possible reduction in the coeff. of expansion, an alloy was obtained with $\alpha \times 10^6 = 0{\cdot}028 - 0{\cdot}002328\theta$. A kilometre wire of this metal—called *invar*—contracts less than 0·4 mm. in passing from 0° to 20°; and a comparison of the elongation of platinum, invar, and 0·06 per cent. carbon steel when warmed from 0° to 10° gave the respective values 88·6μ, 0·05μ, and 121μ; from 0° to 20°, respectively 177·6μ, —0·36μ, and 242μ; and from 0° to 30°, respectively 266·9μ, —1·26μ, and 364μ.

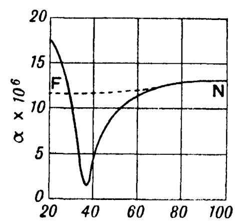


FIG. 219.—The True Coefficient of Expansion of Nickel-Steel at 20°.

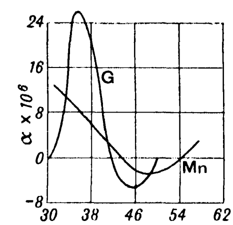


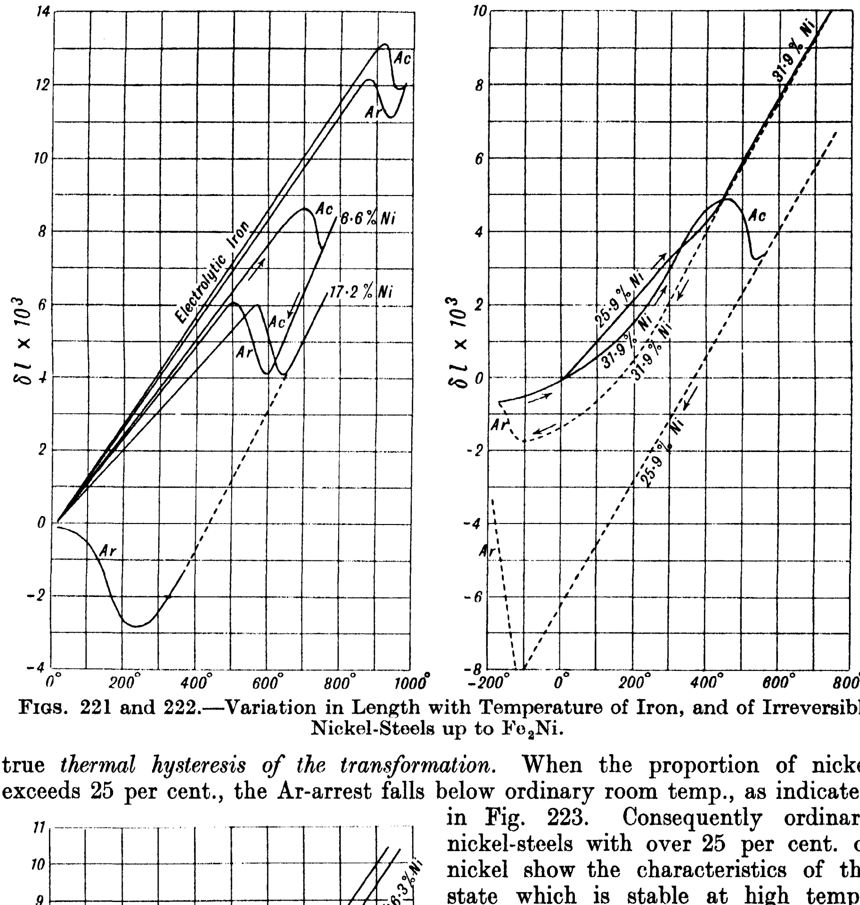
FIG. 220.—The Effect of Chromium and Manganese on the Expansion of Nickel-Steel.

P. Chévenard studied a series of forged nickel alloys with 0 to 98 per cent. of nickel—and less than 0·05 per cent. carbon, less than 0·10 per cent. silicon, and a total percentage of foreign elements not exceeding 0·5 to 0·7. The specimens were cooled sufficiently to transform them into the state which is stable at low temp. Some after being cooled by liquid hydrogen at —253°, were found to have permanently expanded:

Ni . . .	25·9	29·2	30·6	31·9	33·5	34·1	35·4 per cent.
Expansion .	7·6	5·5	5·0	1·2	0·3	imperceptible	mm. per metre

The change with the 31·9 per cent. alloy was exactly the same as if the cooling had been effected at —195°, so that the transformation with this alloy, beginning at about —125°, is completed at —195°. This means that the vanishing of the irreversible elongation cannot be ascribed to the failure of the cooling to effect complete transformation. In accord with the conclusion of P. Weiss and G. Foëx, P. Chévenard concluded that the limit of the irreversible alloys corresponds with the compound Fe_2Ni with its 34·45 per cent. of nickel. This conclusion is said to be in accord with the curves, Figs. 221 and 222, for the effect of changing the temp. in the directions of the arrows on the elongations on irreversible steels. With purified iron, the Ac- and Ar-arrests, which mark the beginning of the transformation respectively on heating and cooling, differ by but a few degrees, but the addition of nickel produces a lowering of the Ac-transformation, and a considerable increase in the difference between the Ac- and the Ar-arrests. The result for any given alloy depends on the condition of cooling, and on the rate of change

of temp. By conducting the experiment more and more slowly, the difference between the Ac- and the Ar-arrests approaches a finite limit which represents the



FIGS. 221 and 222.—Variation in Length with Temperature of Iron, and of Irreversible Nickel-Steels up to Fe_2Ni.

true *thermal hysteresis of the transformation.* When the proportion of nickel exceeds 25 per cent., the Ar-arrest falls below ordinary room temp., as indicated in Fig. 223. Consequently ordinary nickel-steels with over 25 per cent. of nickel show the characteristics of the state which is stable at high temp., and behave quite differently from the steels containing less nickel which are normally in the state stable at low temp. In the alloy with 31·9 per cent. nickel, the Ar-transformation temp. is at —125°. As the proportion of nickel approaches that of Fe_2Ni, the range of temp. accompanying the irreversible transformation diminishes and approaches zero as a limiting value. Alloys with between 34·45 per cent. nickel, Fe_2Ni, and 67·75 per cent., $FeNi_2$, are reversible, and have expansion curves like those discussed in connection with Fig. 217, and illustrated by the group of curves in Fig. 223. An alloy with 35·4 per cent. of nickel, approximating to invar, expands normally

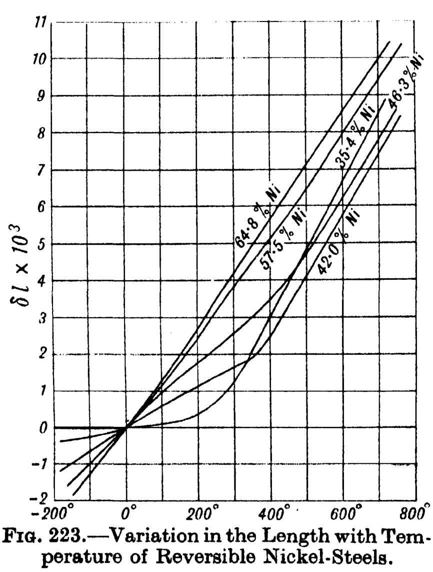


FIG. 223.—Variation in the Length with Temperature of Reversible Nickel-Steels.

above 200°. The variation in the true coeff. of expansion of these alloys, with

temp., is shown in Fig. 224, which illustrates how the anomaly changes progressively with composition. The curves for the variation in length and the true coeff. of expansion for an alloy, very nearly Fe_2Ni, are shown in Fig. 225;

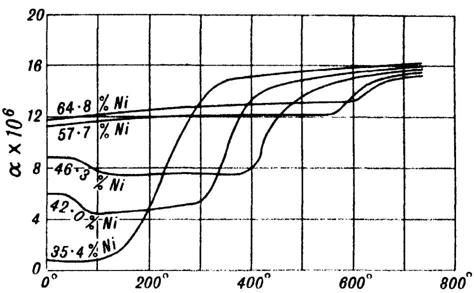


FIG. 224.—Variation of the True Coefficient of Expansion with Temperature.

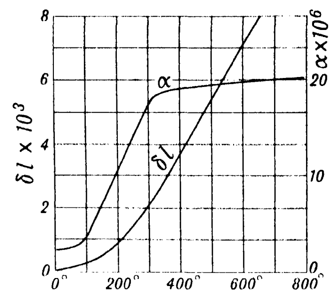


FIG. 225.—Variation of Length and of the True Coefficient of Expansion with Temperature.

and this alloy is the only one of the group which does not show a bend corresponding to *BC* of Fig. 217. That is, the true coeff. of expansion always decreases on cooling down to at least —125°. The bend *BC* appears in the alloy with 35·4 per cent. of nickel, and the curve of the true coeff. of expansion has the minimum characteristic of invar. Consequently, the reversible anomaly gradually disappears as the alloy approaches the composition of $FeNi_2$—67·75 per cent. nickel.

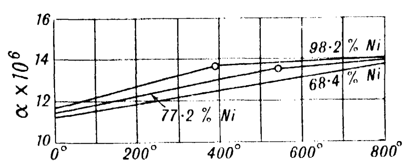


FIG. 226.—Variation of the True Coefficient of Expansion with Temperature for Reversible Nickel-Steels between $FeNi_2$ and Ni.

A. L. Colby also observed that abrupt changes occur in the coeff. of expansion as the ferromagnetic properties disappear on heating. P. Chévenard observed that the iron-nickel alloys between $FeNi_2$ and Ni also show expansion anomalies of a similar kind, they decrease with the addition of iron to nickel, and disappear completely when 32·25 per cent. of iron, corresponding with $FeNi_2$, has been added. The change of the true coeff. of thermal expansion with temp. with these alloys can be represented by two straight lines meeting at the Curie point, Fig. 226. The alloy having the composition $FeNi_2$ is the only one which can be represented by a single parabolic function of the temp. between 0° and 800°. P. Chévenard gave the *résumé* in Fig. 227 of his observations on the variation with temp. of the true coeff. thermal expansion of nickel-steels. The alloys containing less than 34·45 per cent. of nickel are stable at high temp. in the state which is reversible.

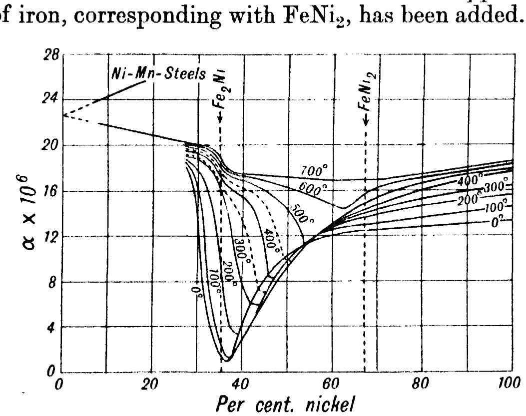


FIG. 227.—Variations in the True Coefficient of Linear Expansion of Nickel-Steels at Different Temperatures.

The curve at 0° resembles that of C. E. Guillaume's Fig. 219, the curve at 700° begins at a point corresponding with 5 per cent. of nickel because at this temp. alloys with a less proportion of nickel do not exist in a state which is stable at a

high temp. This curve is almost a straight line, and if it be prolonged backwards it cuts the ordinate for pure iron at the same point as the prolongation of the line resulting from measurements on nickel-steels containing considerable proportions of manganese. P. Chévenard said that this point represents hypothetically the true expansion coeff. of γ-iron at 700°.

C. E. Guillaume's, and P. Chévenard's theory of the phenomena shown by the iron-nickel alloys is as follows: The irreversible phenomena are associated with the transformation of iron; the reversible anomaly, with a modification of nickel diferride, Fe_2Ni. While the external manifestations of these phenomena show such common features as reduction of vol. and increase of rigidity on warming, there is an essential difference between the two. The irreversible transformation involves an inner molecular reaction between the two solid soln.: $(\alpha\text{-}Fe+Fe_2Ni) \rightleftharpoons (\gamma\text{-}Fe+Fe_2Ni)$, each of which can exist within a certain zone of temp. The right and left members of the reaction involve two different phases, and the passage from one to the other is accompanied by a change in crystalline structure. The anomaly attending the reversible transformation involves a progressive and reversible modification in the properties of the alloys which is spread over a large interval of temp., reaching a maximum in the neighbourhood of the composition Fe_2Ni, and gradually disappearing on approaching $FeNi_2$. The composition $FeNi_2$ forms a kind of boundary between the anomalous reversible alloy, and those showing the peculiarities of nickel. C. Benedicks and N. and G. Ericsson employed a similar hypothesis. C. Benedicks and P. Sederholm, and K. Honda and H. Takagi attribute the non-expansibility of invar to the fact that the high proportion of nickel lowers the A_3-transformation to room temp. and at the same time makes the γ- to α-transformation a progressive one. C. Benedicks, however, added that the position of the Ac_3-transformation for 36 per cent. of nickel is about 400°, and that of the Ar_3-transformation, about $-100°$. Hence, equilibrium would be impossible at ordinary temp. and invar would be decidedly unstable. This is not in agreement with observations. T. Kase, however, showed that invar is not a compound but a γ-solid soln.; and that the A_3-transformation takes place below the temp. of liquid air. K. Honda and S. Miura showed that the abnormal property of invar has no connection with the A_3-transformation, but is based on the property of the ferromagnetic alloy in the γ-phase. G. Phragman inferred that the anomalous expansion is not due to a two-phase reaction but is rather a property of the face-centred cubic lattice of these alloys when containing about 38 per cent. of nickel. This implies that the low coeff. of expansion is not due to a two-phase reaction which compensates the normal dilation of the two phases, as assumed by C. Benedicks and P. Sederholm. There is scarcely any reason to assume the presence of a body-centred, cubic phase in the low expansion alloys. C. Benedicks based a theory of the expansion anomaly on the assumptions that the alloy contains two definite phases—*vide supra*—that, on heating, a certain proportion of one phase changes into the other, and that this transformation is accompanied by a contraction. The observed thermal expansion is the difference between the normal thermal expansion and the contraction due to the transition from one phase to another; if the two are equal in magnitude, one compensates the other, and no change in vol. occurs. It is assumed that the one phase is in an extremely finely-divided state so that the surface between the two phases is a very large one; otherwise an excessive time would be required to reach equilibrium. The times required for the two changes to occur, when the temp. is raised abruptly, is not necessarily the same. C. Benedicks showed that the true thermal expansion is very rapid, while the two-phase transformation is slower, so that with a rapid heating, the first expansion which occurs during the first 3 minutes is normal—lying between that of iron, $0{\cdot}0_412$, and that of nickel, $0{\cdot}0_413$; thereafter a considerable contraction occurs and decreases in intensity relatively slowly, and ceases only after the lapse of 12 minutes. The resultant or apparent expansion was thus reduced from $0{\cdot}0_413$ to the normal value for invar $0{\cdot}0_64$ in 12 minutes.

The hysteresis attending the phase transformation shows that the initial expansion of invar is a function of time. H. Masumoto noticed that the γ-solid soln. has a smaller expansibility in the ferromagnetic state than it has if it be in the paramagnetic state. The **ferromagnetic expansion** curve at 20° is shown in Fig. 228. The saturation value of the iron-nickel alloys has a deep minimum at 30 per cent. of nickel, and the critical point of nickel is raised to a maximum with 35 per cent. of iron and subsequently decreases down to 30 per cent. of nickel, so also does the magnetization increase at first rapidly and then slowly as the temp. falls from the critical point downwards, and, as the critical point rises, so does (i) the magnetization at ordinary temp. increase; and (ii) the magnetization increase as the proportion of iron in nickel increases. Hence, the maximum of the magnetization curve is displaced towards the iron side as compared with the critical point. The ferromagnetic expansion, e, is proportional to the saturation magnetization, I_0, at room temp. for γ-solid soln. of varying concentration, so that $e=kI_0$. In Fig. 229, RQP is the thermal expansion curve; OR, the ferromagnetic expansion; the ratio $QS : RS$ denotes the mean coeff. of thermal expansion, α; and OA_2, the critical temp. Θ. Then,

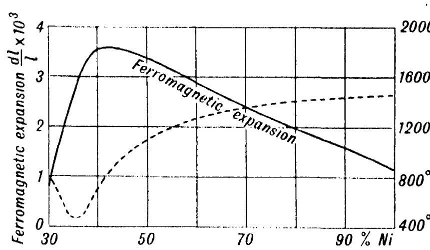


FIG. 228.—Ferromagnetic Expansion of Ni-Fe Alloys.

$$\alpha=\frac{QS}{RS}=\frac{QA_2-SA_2}{\Theta}=\tan\delta-\frac{kI_0}{\Theta}$$

Whether or not α has a deep minimum depends on the ratio $I_0 : \Theta$, and this ratio can be calculated from the magnetic data. The result furnishes a curve, dotted in Fig. 229, which has the characteristics of the thermal expansion curve. The small expansibility of the invar alloys can thus be explained from purely magnetic data. The subject was discussed by T. F. Russell. O. Bauer and H. Sieglerschmidt observed that 0·48 per cent. of nickel had no effect on the thermal expansion of cast iron, but it reduced the permanent elongation.

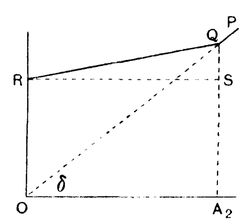


FIG. 229.

The thermal expansion of the nickel alloys, *e.g.*, invar, is very sensitive to the previous history of the alloy, and C. E. Guillaume stated that *l'extrême sensibilité de invar aux traitements est un phénomène curieux en lui-même, et qui semble à peu près isolé.* A **thermal after-effect** or *Nachwirkung* similar to that observed with glass—**6.** 40, 37—occurs, and the length of a bar of the alloy following a variation of temp. depends, at least in the beginning, on the temp. to which it has previously been subjected, and on the rapidity with which the final temp. has been attained. This is not the same phenomenon as the hysteresis observed by C. Benedicks although it supports his hypothesis. Consider a forged bar in a state corresponding with CD, Fig. 217, and suppose that its dimensions are measured from time to time while its temp. is maintained constant. If the bar has previously been exposed to a higher temp., it will first complete the main contraction accompanying the attainment of the temp. equilibrium, and afterwards slowly elongate a little with time; on the other hand, if the bar has been previously treated at a lower temp., it will contract. The duration of the recovery is always greater when the final temp. is reached by cooling, than when it is attained by heating. In either case, the higher the temp. the greater is the speed of the change. In illustration, C. E. Guillaume found that a metre wire raised to 100° soon after forging elongates at the rate of $0{\cdot}06\mu$ per minute, but if the alloy has been allowed

to season, age, or rest at room temp. for a long time, it contracts at the rate of 0·8 to 0·9μ per min. If it be heated to 15° soon after forging, it elongates at the rate of 0·07 to 0·09μ per day; and if raised to 15° after annealing at 40°, it elongates at the rate of 0·03μ per day. Again, after a long rest at room temp., the contraction at 100° is completed in about half an hour, but it occupies several days at 40°. These changes recall those which occur with chemical changes where the state of equilibrium depends on the temp. These variations in length make the thermal expansion of invar indeterminate between two limits, one corresponding to a rapid attainment of the final temp., and one corresponding to a long rest at this temp. According to J. R. Benoît and C. E. Guillaume, for a temp., $\theta°$, between 0° and 100°, the difference between these two limits is represented by the empirical formula $\delta l/l = -0{\cdot}0_8325\theta^2$. The result is summarized in Fig. 230, and the observed results for $\delta l/l \times 10^6$ are as follow:

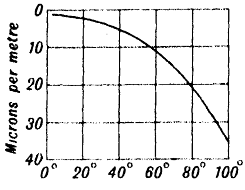


FIG. 230.—Temporary Variations in the Length of Invar following Rapid Changes of Temperature.

At starting	0°	1°	5°	10°	15°	20°	25°	29°
Starting from 0°	0·0	0·0	−0·1	−0·3	−0·7	−1·3	−2·0	−2·7
Starting from 15°	0·7	0·7	+0·6	+0·4	0·0	−0·6	−1·3	−2·0

Besides the transient changes just indicated, there are other permanent changes which continue a long time at a constant temp. Thus a bar of invar left to itself at any constant temp. gradually elongates slightly at first rapidly and then more and more slowly as it approaches asymptotically a definite length. The rate of ageing increases with temp. C. E. Guillaume reduced this change to a minimum by using an ageing process, or heat treatment, or tempering, which he called *étuvage*—steaming or stewing—in order to distinguish it from ordinary annealing—*recuit*. In the process of tempering, the forged bars were subjected to a series of slowly decreasing temp. starting at 100° and ending at 20° to 25° after an interval of 2 or 3 months.

The effects of the heat-treating of forged bars are illustrated by Fig. 231, which represents the elongations observed during a period of 4500 days with a bar of invar cooled in air after forging at a red-heat, and then maintained almost constantly below 20°. The lower curve represents the changes with a similar bar previously reheated to 150°, and then cooled in 50 days to 40°. The same alloy cooled gradually for several weeks more down to 25°, afterwards elongates in accord with the same curve but starting from a point corresponding with 100 days and 3μ per metre. Similar curves have been drawn for quenched or drawn bars, or wires, kept in the laboratory after being very slowly cooled from 100° to 25°. Rest at a higher temp. has continued the effect of previous heatings, and accelerated the elongation. The thermal expansion of invar is increased a little by the very slow cooling of the specimen. After the ageing is completed, the expansivity remains constant for a long period. Quenching lowers the expansivity of invar. If $\delta\alpha$ denotes the difference between each value observed and the normal value, about $1{\cdot}2\times10^{-6}$, in *l'état naturel*, then, C. E. Guillaume found that for a rod annealed at 900° and cooled in the furnace, $\delta\alpha = 0{\cdot}65\times10^{-6}$; for a rod annealed at 900° and cooled in air, $\delta\alpha = 0{\cdot}26\times10^{-6}$; for the same rod reheated and cooled in air, $\delta\alpha$=zero; a 24-mm. bar quenched from 900°, $\delta\alpha = -0{\cdot}42\times10^{-6}$; a 12-mm. bar quenched from 900°, $\delta\alpha = -0{\cdot}46\times10^{-6}$; an 8-mm. rod quenched from 900°, $\delta\alpha = -0{\cdot}49\times10^{-6}$; and a 1·65-mm. wire quenched from 900°, $\delta\alpha = -0{\cdot}53\times10^{-6}$. Drawn bars behave a little differently from forged ones. The first reheating to 100° produced an elongation for several hours followed by a contraction. At lower

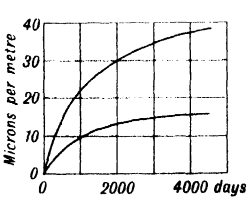


FIG. 231.—The Expansion of Invar with Time.

temp. they behaved like forged bars even if the contraction at 100° had scarcely commenced. A drawn bar kept for a long time at the room temp., and then brought to 100°, shortened for perhaps half an hour, then lengthened for several hours, and finally shortened again for more than 100 hrs. There are thus three distinct variations in the same bar, and these differ in magnitude and duration, the first two resemble those observed with forged bars, but the third is peculiar to drawn bars. J. R. Benoît and C. E. Guillaume found that a drawn and forged bar gradually cooled from 100° to 20° in 3 months elongated, in δl microns per metre, as follows :

Days .	0	100	500	1000	1500	2000	2500	2900
δl .	0·0	1·5	4·4	6·6	8·1	9·3	10·1	10·8μ

A wire to be used for geodetic measurements is rarely in a suitable condition for calibration until 4 or 5 months later. Daily variations of temp. are considered to be abrupt, while seasonal variations of temp. are considered to be very slow. Thus, if invar were used for geodetic measurements, the mean temp. of the weeks immediately preceding would be considered as being attained slowly, whereas the equation for thermal expansion is based on rapid changes of temp. If, therefore, the mean temp. of the season were 20°, and the equation for thermal expansion had been determined, after a long rest, at 12°, a correction is required for the temp. of the moment by the expansion formula obtained during the calibration, and also a correction by the formula $\delta l/l = -0{\cdot}00325 \times 10^{-6}\theta^2$.

C. E. Guillaume found that at a given temp., the instability of the nickel alloy is greater the nearer this temp. is to that at which the alloy loses its magnetic qualities. At ordinary temp., the stability with respect to variations of time and temp. is increased by adding nickel up to a maximum of about 43 per cent. ; on exceeding this proportion, the direction of the change in length is reversed ; and the contraction with time increases slightly on adding still more nickel. For example, the length of a bar with 43·6 per cent. nickel was measured immediately after forging, and then gradually cooled from 100° to 30° for 3 months. The length was thus reduced only 0·7μ per metre ; similarly, a bar with 44·2 per cent. nickel contracted 2·6μ per metre in 66 hrs. at 100° immediately after forging, and it then contracted 0·4μ more during 2000 days, and 1·1μ during 4000 days at room temp. ; while a bar with 56·2 per cent. nickel was similarly shortened 8·8μ by keeping it 130 hrs. at 100°, and subsequently, 2·5μ by keeping it 2000 days at room temp. The alloy with 46 per cent. nickel is preferred for making standards of lengths because it has a greater stability than invar, it also offers a greater resistance to oxidation, and it has a thermal expansivity appreciably less than that of platinum. An alloy with 56 per cent. nickel has an expansivity about the same as that of steel, and it is more stable, and less subject to corrosion. It is therefore used in industrial measuring instruments to avoid temp. corrections.

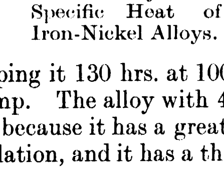


FIG. 232.—Thermal Conductivity and Specific Heat of Iron-Nickel Alloys.

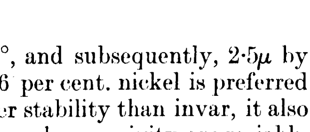


FIG. 233.—The Specific Heat of Nickel-Iron Alloys.

L. R. Ingersoll found the **thermal conductivity,** k, of the iron-nickel alloys between 20° and 100°, and found, in c.g.s. units,

Nickel	0	1·07	10·20	19·21	25·2	35·09	47·08	75·06	100 per cent.
k .	0·1428	0·1035	0·0687	0·0502	0·0320	0·0262	0·0367	0·1181	0·1168

The results are plotted in Fig. 232. W. C. Ellis and co-workers gave 0·0329 cal. per cm. per sec. per degree for the thermal conductivity of the Fe : Ni (70 : 30) alloy ; and 0·0324 for the Fe : Ni : Cr : Mn (68 : 29 : 2 : 1) alloy. K. Honda found for nickel-steel, made from iron with 0·09 per cent. of carbon, 0·11, Si ; 0·31, Mn ;

0·03, P; 0·026, S; and 0·288, Cu; and nickel with 0·29 per cent. carbon, 0·15, Si; 0·35, Mn; 0·017, S; 4·20, Cu; 1·25, Fe; and 0·24, Co, the values, at 30°, of k_1, for specimens annealed once at 900°, and k_2, for specimens once cooled in liquid air:

Ni . . .	0	4·6	9·2	21·2	23·6 per cent.
k_1 . . .	0·0980	0·0764	0·0616	0·0409	0·0310
k_2 . . .	0·0980	0·0722	0·0609	0·0450	0·0460
Ni . . .	27·7	32·8	55·4	73·8	92·3 per cent.
k_1 . . .	0·0199	0·0193	0·0360	0·0563	0·0833
k_2 . . .	0·0449	0·0193	—	—	—

The results are plotted along with the electrical resistances in Fig. 235. M. Jakob made some observations on the subject. L. R. Ingersoll measured the **specific heat** of the iron-nickel alloys, in cals. per gram, between 25° and 100°, and found:

Nickel .	1·07	10·20	19·21	25·20	35·09	47·08	75·06	100 per cent.
Sp. ht. .	0·1162	0·1168	0·1162	0·1181	0·1228	0·1196	0·1181	0·1168

The results are plotted in Fig. 233. W. C. Ellis and co-workers gave 0·116 for the sp. ht. of the Fe : Ni (70 : 30) alloy; and 0·114 for the Fe : Ni : Cr : Mn (68 : 29 : 2 : 1) alloy. M. Kawakami measured the sp. ht. of the iron-nickel alloys, and his results are summarized in Fig. 233, where the continuous curve refers to the annealed alloy; the broken curve to the alloy cooled in liquid air; and the dotted line to the quenched alloy. M. Garvin and A. M. Portevin studied the cooling curves. According to W. Brown, the sp. ht. of some nickel-steels with 5·04 per cent. manganese and 0·6 per cent. carbon, and with 14·35, 19·01, and 25·00 per cent. of nickel, were respectively 0·1208, 0·1194, and 0·1186 A. Dumas' results are summarized in Fig. 234.

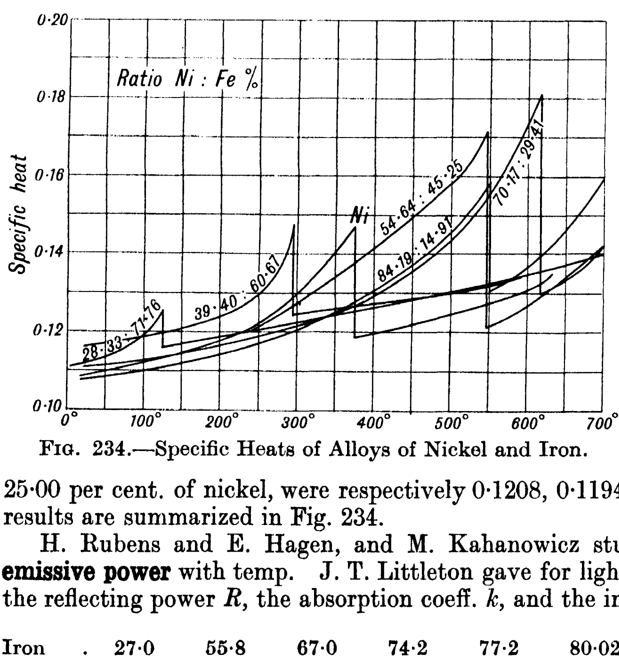


FIG. 234.—Specific Heats of Alloys of Nickel and Iron.

H. Rubens and E. Hagen, and M. Kahanowicz studied the changes in the **emissive power** with temp. J. T. Littleton gave for light of wave-length 5893 A., the reflecting power R, the absorption coeff. k, and the index of refraction μ,

Iron .	27·0	55·8	67·0	74·2	77·2	80·02	93·77	98·30 per cent.
R .	62·0	60·9	60·1	59·4	58·8	58·8	58·3	58·8
k .	3·50	3·52	3·35	3·42	3·41	3·40	3·34	3·44
μ . .	2·01	2·16	2·23	2·25	2·30	2·31	2·38	2·44

S. Loria and C. Zakrzewsky measured the index of refraction of invar; and S. Loria and C. Zakrzewsky found that for invar, with light of wave-length λ,

λ . .	4390	4475	4663	5025	5513	5896	6483	7040
k . .	2·43	2·48	2·60	2·74	2·92	3·08	3·21	3·42
μ . .	1·57	1·64	1·72	1·83	1·98	2·05	2·25	2·43

P. D. Foote studied the Kerr effect with invar; S. J. Barnett, the gyromagnetic effect with permalloy; W. Kraemer, the spectrum; and K. Hayakawa, the emission of electrons.

P. R. Kosting obtained the results summarized in Fig. 235 for the electrical resistance of nickel-iron alloys in microhms per cm. cube at 20°, and for the temp. coeff. of the alloys in ohms per ohm per degree $\times 10^4$.

C. E. Guillaume gave for the change of **electrical resistance** of iron-nickel alloys between 0° and $\theta°$, for 26·2 per cent. nickel, $(844+0{\cdot}01\theta)10^{-6}$; for 28·7 per cent. nickel, $(700-0{\cdot}20\theta)10^{-6}$; for 30·4 per cent. nickel, $(897-0{\cdot}43\theta)10^{-6}$; for 35·0 per cent. nickel, $(1561-1{\cdot}69\theta)10^{-6}$; for 35·7 per cent. nickel, $(1161-1{\cdot}68\theta)10^{-6}$; and for 22·0 per cent. nickel with 3 per cent. chromium, $(784-0{\cdot}13\theta)10^{-6}$. He did not find any marked differences in the electrical resistances of various nickel-steels; all those studied ranged from 80 to 90 microhms at ordinary temp. Nor did he find any anomalies, corresponding with anomalies in other physical properties, between 20° and 150°. On the other hand, J. Hopkinson, O. Boudouard, and A. P. Schleicher and W. Guertler found anomalies in the electrical resistances with changes of temp. The subject was studied by E. D. Campbell and H. W. Mohr, P. Chévenard, O. Dahl, H. A. Dickie, W. T. Griffiths, W. C. Hirsch, M. A. Hunter and co-workers, J. T. MacGregor-Morris and R. P. Hunt, A. de Negri, W. Phillips, F. Ribbeck, R. Schenck, A. P. Schleicher and W. Guertler, A. Schulze, and G. Tammann and V. Caglioti. The results of G. Gossels, and L. R. Ingersoll are summarized in Fig. 236. W. C. Ellis and co-workers gave $k\times10^{-5}$= 0·1052 mho for the electrical conductivity of the Fe : Ni (70 : 30) alloy; and $k\times10^{-5}$=0·1071 mho for the Fe : Ni : Cr : Mn (68 : 29 : 2 : 1) alloy. L. R. Ingersoll found the sp. electrical resistance of nickel-iron alloys, R microhms per cm. cube, at 20° to be:

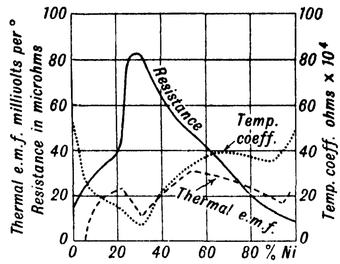


FIG. 235.—Electrical Resistance of Nickel-Iron Alloys.

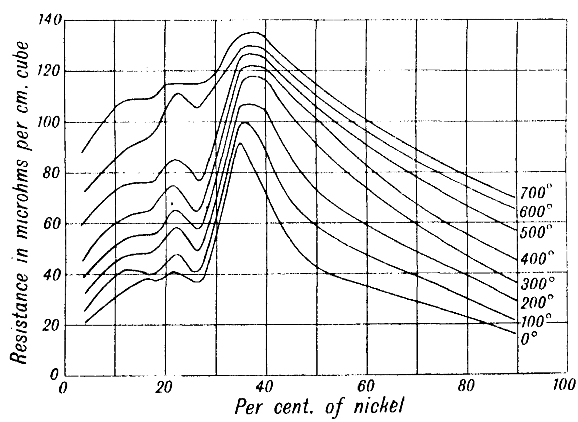


FIG. 236.—The Effect of Temperature on the Resistance of the Nickel-Iron Alloys.

Ni	4·0	7·0	13·0	22·11	26·40 per cent.
R	20·9	25·2	33·0	40·0	35·9
a	0·0020	0·0023	0·0018	0·0018	0·0016

Ni	35·09	40·0	47·08	90·0 per cent.
R	92·0	74·1	47·5	15·5
a	0·0011	0·0022	0·0036	0·0034

The temp. coeff. a, between 0° and 100°, are also indicated. The results for temp. up to 700° are summarized in Fig. 237. For nickel-iron alloys the resistances, R, in microhms per cm. cube, observed by C. F. Burgess and J. Aston, were:

Ni	0	0·27	7·05	10·20	22·11	25·20	28·42	35·09	75·06	100 per cent.
R	12·1	13·1	26·9	28·6	38·7	63·2	82·0	81·1	22·1	12·4

There is a maximum corresponding with Fe_2Ni. J. Hopkinson's observations on the variation of the resistance of an irreversible nickel-steel with 25 per cent. nickel are summarized in Fig. 238. F. Ribbeck studied the effect of composition,

temp., and heat treatment on the electrical resistance of nickel-steel. G. J. Sizoo and C. Zwikker observed that the conductivity curve—mhos per cm. cube—with single crystals of nickel-iron alloys has ill-defined maxima at Fe_3Ni and $FeNi_2$, and minima at Fe_2Ni, and at 90 per cent. nickel. The temp. coeff. α between 0° and 100° has maxima and minima at the same points.

Nickel .	0	10·1	20·4	33·6	40·8	70·0	79·8	90·9	100 per cent.
Mho $\times 10^{-4}$.	9·75	3·68	3·61	1·31	1·79	7·30	7·46	8·26	13·8
$\alpha \times 10^5$.	580	225	260	126	306	592	560	454	617

H. Tomlinson gave for the sp. electrical resistance, R, at 20°, in c.g.s. units for hard-drawn and annealed iron-nickel wires, as well as for the alteration in sp. resistance, δR, produced by a longitudinal traction of a gram per sq. cm., and the alteration, δR, produced by a longitudinal magnetic force of a c.g.s. unit:

Nickel	0	22	25	30	100 per cent.
R Hard-drawn . . .	12,090	47,980	60,944	55,080	17,570
R Annealed . . .	10,740	75,080	78,723	72,913	17,360
$\delta R \times 10^{10}$ by traction . .	+13·23	+7·53	+6·64	−1·34	−40·80
$\delta R \times 10^6$ by a magnetic field .	+23·35	+3·06	+1·48	+4·56	+80·70

One of L. Anastasiadis and W. Guertler's curves is shown in Fig. 239. The results with the heating and cooling are not reversible. P. W. Bridgman found that the effect of pressure on the sp. resistance, R, of the nickel-iron alloys can be

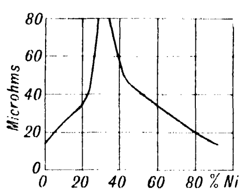


FIG. 237.—The Electrical Resistance of Nickel-Iron Alloys.

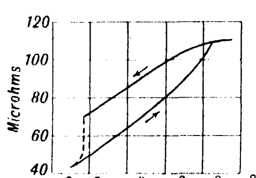


FIG. 238.—The Electrical Resistance of Nickel-Steel at Different Temperatures.

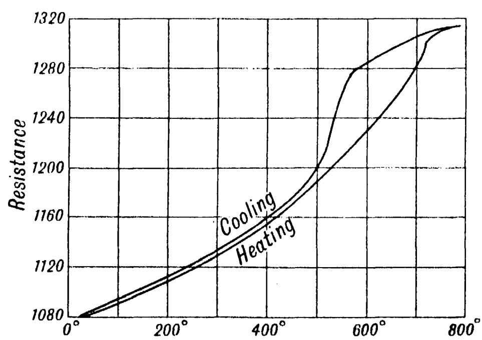


FIG. 239.—The Electrical Resistance of an Iron-Nickel Alloy on Rising and Falling Temperatures.

represented by $\delta R/R_0 = ap + b_{p2}$, where a and b are constants, and he also gave values for the temp. coeff., α, between 0° and 100°:

Ni . .	0	10	25	30	40	50 per cent.
30° $a \times 10^6$.	−2·427	0·036	2·822	8·7	9·100	5·904
30° $b \times 10^{11}$	1·14	−8·0	−0·92	—	−6·06	5·62
75° $a \times 10^6$.	−2·450	−0·091	2·315	7·7	6·910	5·422
75° $b \times 10^{11}$	1·00	−3·00	−0·92	—	−7·08	3·68
R (30°) .	10·5	30·1	32·4	51·4	65·6	41·9
$\alpha \times 10^3$.	6·21	2·31	2·62	5·89	2·87	4·43

Ni . .	60	75	78·5	81	100 per cent.
30° $a \times 10^6$.	3·002	0·456	−0·129	−0·389	−1·905
30° $b \times 10^{11}$	2·29	—	—	—	0·50
75° $a \times 10^6$.	2·886	0·394	−0·181	−0·461	−1·925
75° $b \times 10^{11}$	1·70	—	—	—	0·56
R (30°) .	30·7	18·9	18·2	17·1	7·0
$\alpha \times 10^3$.	4·74	6·28	4·62	4·46	6·34

The results are plotted in Fig. 240. There are breaks in the curves as the alloys with over 25 per cent. of nickel change from the body-centred to the face-centred cube. J. Hopkinson found that by the intense cooling of steel with about 25 per cent. nickel, the electrical resistance at room temp. was changed from 72 to 52 microhms. T. D. Yensen obtained a curve showing a maximum with about 30 per cent. nickel. K. Honda compared the electrical and thermal conductivities of the nickel-steels made from the metals indicated above in connection with the thermal conductivities. The electrical conductivities K_1 mho refer to specimens annealed once at 900°, and K_2 mho refer to specimens cooled once in liquid air. The ratios of the two conductivities k_1/K_1 and k_2/K_2 are also indicated :

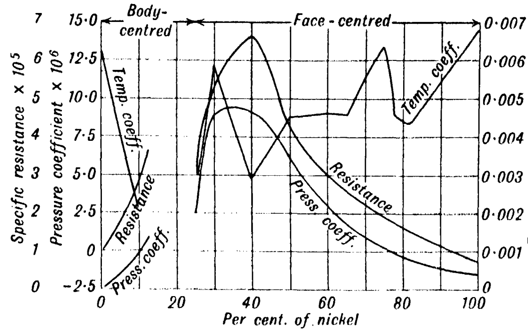


FIG. 240.—The Effect of Pressure on the Electrical Resistance of the Ni-Fe Alloys.

Ni .	0	4·6	9·2	21·2	23·6	27·7	32·8	55·8	73·8	92·3 per cent.
K_1 .	0·504	0·362	0·281	0·201	0·182	0·107	0·101	0·256	0·365	0·500
K_2 .	0·504	0·364	0·276	0·220	0·233	0·240	0·101	—	—	—
k_1/K_1	1·94	2·11	2·19	2·04	1·70	1·86	1·91	1·41	1·54	1·64
k_2/K_2	1·94	1·98	2·20	2·03	2·01	1·87	1·91	—	—	—

The results are plotted in Fig. 241. The minima for the two electrical conductivities lie at concentrations approximating 30 per cent. of nickel. There are small minima and maxima, respectively at 21 and 27 per cent. of nickel, for the specimens cooled once in liquid air. The ratio of the thermal and electrical conductivities is never a constant for all nickel-steels, but the deviation is not large when the variations of the conductivities amongst themselves are considered. It is more correct to say that the ratio has nearly a constant value for alloys either above or below 31 per cent. of nickel—the mean values being respectively $1·98 \times 10^{-6}$ and $1·68 \times 10^{-6}$. H. C. H. Carpenter and co-workers found for nickel-steels with about 0·45 per cent. of carbon and 0·9 per cent. of manganese, the following values, R microhms, at 17° :

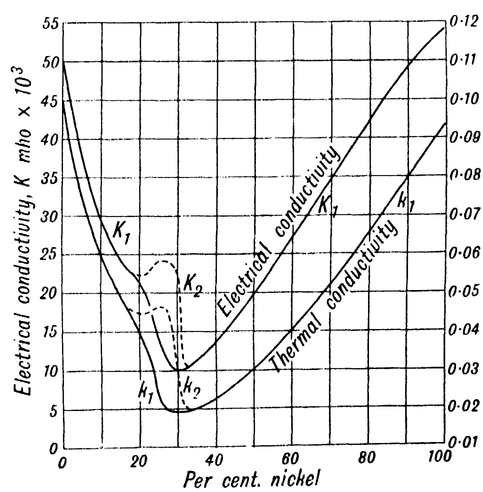


FIG. 241.—Thermal and Electrical Conductivities of Nickel-Steels.

Ni .	0	1·20	2·15	4·25	4·95	6·92	7·95	12·22	15·98	19·98 per cent.
R .	20·3	22·6	24·8	29·1	39·3	42·8	43·9	50·5	63·3	75·4

There is an abrupt change in the resistance of the alloys with from 4·95 to 7·95 per cent. nickel; the other values lie on a linear curve. Measurements were also made by H. le Chatelier, E. Sedström, G. A. Roush,

C. Benedicks, A. Schulze, R. A. Hadfield, W. F. Barrett and co-workers, J. A. Fleming and J. Dewar, J. A. Fleming, H. C. H. Carpenter and co-workers, A. P. Schleicher and W. Guertler, R. Ruer and L. Schüz, S. F. Schemtschuschny and co-workers, H. Neumann, D. and H. E. Hanson, W. Bein, T. D. Yensen, F. Ribbeck, C. F. Burgess and J. Aston, G. Gossels, etc. A. M. Portevin found an increase in the resistance of iron of 1·51 microhms; and K. Honda, 1·5 microhms per cm. cube on adding 1 per cent. of nickel. O. Boudouard gave for the resistance R microhms:

0·1 per cent. C	Ni	2·23	5·23	10·10	15·17	20·40	25·85 per cent.
	R	15·8	22·1	27·8	31·1	33·7	39·8
0·8 per cent. C	Ni	2·20	4·90	9·79	15·04	20·01	29·96 per cent.
	R	20·1	26·2	40·6	47·8	60·9	87·1

A. M. Portevin said that the influence of nickel reveals itself by an increase in the sp. electrical resistance which varies with the percentage of carbon and the microstructure of the steel. High values are attained only by the polyhedral steels. Hardening produces an increased resistance only in steels which in the normal state are pearlitic, and in those martensitic steels containing 0·8 per cent. of carbon. Generally speaking, the passage from one structure to another is increased by a change in the direction of the curve which represents the variations of sp. resistance as a function of the percentage of nickel. C. Benedicks' formula is not applicable for steels containing over 2 per cent. of nickel. C. E. Guye and A. Schidloff found that the influence of a magnetic field on the electrical resistance is greater with nickel-steel than it is with iron alone. M. Medici, W. E. Williams, D. H. Arnold and L. W. McKeehan, L. W. McKeehan, and D. S. Steinberg and F. D. Miroschnitschenko studied the effects of tension and magnetization on the electrical resistance of permalloy. For G. W. Elmen's observations, *vide infra*, Figs. 243 to 245.

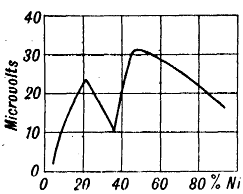


FIG. 242.—The Thermoelectric Force of Nickel-Iron Alloys against Copper.

C. G. Fink and C. M. de Croly found the **electrode potentials** of nickel-iron alloys against sulphuric acid of the percentage composition:

		H_2SO_4	0·45	24·15	53·00	106·5	197·6	395·9	791·6 per cent.
E	98·3 per cent. Ni		−0·420	−0·598	−0·587	−9·548	−0·446	−0·471	−0·480
	78·5 per cent. Ni		−0·638	−0·660	−0·637	−0·626	−0·574	−0·536	−0·512
	52·1 per cent. Ni		−0·710	−0·698	−0·688	−0·660	−0·623	−0·580	−0·571
	37·6 per cent. Ni		−0·720	−0·705	−0·706	−0·690	−0·660	−0·609	−0·578
	Iron		−0·941	−0·916	−0·928	−0·905	−0·872	−0·827	−0·715

H. Tomlinson found the e.m.f. in c.g.s. units of a cell with 22, 25, and 30 per cent. nickel-iron alloys against iron wire, in water at 20°, to be respectively -98×10^5, -149×10^5, and -155×10^5. O. Bauer found the potential of a 25 per cent. nickel-steel in a 1 per cent. soln. of sodium chloride against a normal calomel electrode to be −0·0320 volt at the start; −0·397 volt after 1 hr.; and −0·581 volt after 120 hrs. M. de K. Thompson and A. L. Kaye studied the oxygen and hydrogen over-voltages of the nickel-iron alloys, and also their passivity.

L. R. Ingersoll measured the **thermoelectric force,** E microvolts per degree, of copper against alloys of iron and nickel between 0° and 96°, and the results are summarized in Fig. 242. P. R. Kosting's values are summarized in Fig. 235 along with the resistance curve; the thermoelectric force is expressed in microvolts per degree. E. Steimann observed that the thermoelectric force of a couple of lead and nickel-steel with 36·1 per cent. of nickel is −2461 microvolts between 0° and 100°; and with steel containing 28 per cent. of nickel, the e.m.f. between 20° and 260° is 385 to 386 microvolts. No simple rule was noticed to connect the e.m.f. with the composition. G. Belloc obtained analogous results. W. F. Barrett, and W. Rohn studied the thermoelectric force of the alloys against platinum; and A. Pepe, against iron. O. Boudouard employed the thermoelectric force as a

means of fixing the transition points and obtained the results indicated in Table XVI. E. L. Dupuy and A. M. Portevin gave the results summarized in

TABLE XVI.—THE THERMOELECTRIC FORCE OF NICKEL-STEEL AGAINST COPPER.

Percentage composition		Untreated		Annealed		Hardened	
C (*circa*)	Ni	−80°	100°	−80°	100°	−80°	100°
0·10	2·23	+ 8·8	+ 6·5	+ 8·9	+ 6·3	+10·7	+ 6·2
	7·13	− 4·8	− 7·6	− 4·8	− 7·8	− 4·9	− 7·6
	12·07	−18·1	−17·4	−14·3	−16·9	−14·5	−17·0
	20·40	−27·3	−30·0	−28·4	−30·4	−32·6	−31·3
	30·00	−15·2	− 1·5	−14·8	− 6·9	−14·7	− 1·0
0·20	1·97	+ 8·1	+ 6·3	+ 8·5	+ 7·0	+ 7·9	+ 5·0
	7·59	− 4·3	− 6·8	− 4·1	− 7·3	− 3·2	− 6·0
	12·29	−13·4	−16·4	−13·0	−15·3	−11·7	−15·7
	20·01	−22·0	−21·5	−21·4	−30·6	−22·0	−23·7
	27·87	− 4·1	− 1·9	− 7·9	− 2·3	− 9·2	− 0·9
0·80	2·20	+ 5·7	+ 4·6	+ 6·4	+ 4·7	+ 5·8	+ 4·6
	7·09	− 3·9	− 5·9	− 5·0	− 6·9	− 4·1	− 5·9
	12·27	−10·1	−10·4	− 7·8	− 9·4	− 8·7	− 9·8
	20·01	− 6·8	− 3·5	−12·3	− 6·6	− 5·0	− 5·0
	29·96	− 2·9	− 1·9	− 5·6	− 1·8	− 3·3	− 2·0

Table XVI for the thermoelectric force of nickel against copper between −80° and 0°, and between 0° and 100°. The annealed steel was heated 3 hrs. at 900° and cooled for 7 hrs. in the furnace, and the steel was hardened by heating it to 950° for 13 minutes and quenching it in water at 18°. The steels contained 0·01 to 0·10 per cent. silicon; 0·01 to 0·12 per cent. manganese; and 0·001 to 0·3 per cent. of sulphur. All the curves representing the thermoelectric force in terms of percentage of nickel show a rapid decrease with a clearly marked minimum. This minimum corresponds with the limit between austenitic and martensitic steels. The ascending branch has therefore an affinity with the solid soln. of nickel, carbon, and γ-iron. Similar results were obtained by A. M. Portevin with the electrical resistance of these steels. For O. L. Kowalke's observations on the thermoelectric force of the cobalt and nickel-iron couple, *vide supra*, cobalt. A Schulze, S. Hilpert and F. Herrmann, J. Galibourg, A. Abt, G. Belloc, and P. Chévenard studied the subject. T. S. Fuller gave for the thermoelectric force, E millivolts, against copper, between 0° and 100°, for an alloy of iron with:

Nickel .	0	17	20	30	81·2	93	100 per cent.
E .	+0·86	−0·64	−0·55	−0·52	−2·45	−1·90	−2·38

H. Tomlinson measured the thermoelectric force, E, in c.g.s. units at 20°, the alteration, δE, in the thermoelectric force produced by a longitudinal traction of a gram per sq. cm., and by a longitudinal magnetizing force of a c.g.s. unit:

Nickel	0	22	24	30	100 per cent.
E Hard-drawn	—	−1931	−1451	−434	—
E Annealed	−1862	−1011	−731	−380	−2200
$\delta E \times 10^{10}$ by traction . .	+22	−27	−21	−30	Negative
$\delta E \times 10^{6}$ by a magnetic force	+68·6	−38·9	38·3	−155·0	Negative

A. W. Smith and J. Dillinger, and A. W. Smith observed that a longitudinal magnetic field decreased the thermoelectric force of permalloy; annealing at 1000° increased the change. Tension decreased the thermoelectric force of an alloy with 78 per cent. nickel; an alloy with 81 per cent. nickel was insensitive to tension; and with an alloy with 84 per cent. nickel tension decreased the thermoelectric force at fields below 10 gauss, but for greater fields, an increase occurred; they found that the effect rises to a maximum and then decreases to negative values with

increasing magnetic inductions. This may mean that the Hall e.m.f., ϵ, in the relation $\epsilon = R_0H + R_1I$—*vide* iron—is dependent on a positive value of R_1 and a negative value for R_0 when R_1 and R_0 are the same order of magnitude; or it may mean that in the annealing of the alloys, two magnetically different components are produced with R_1 and R_1 of opposite signs—the iron of permalloy has a positive coeff. and nickel a negative one. The subject was studied by E. M. Pugh. With all the alloys, dE/E was insensitive to tension over 10 kgrms. per sq. mm. E. D. Campbell and H. W. Mohr studied the thermoelectric potential of the alloys. U. Salerno found that the **Hall-effect** is exhibited by the nickel-steel alloys and has the same characteristics as it has with ordinary ferrometals. Invar, for instance, shows a moderately high coeff. of rotation. A symmetry observed in all the alloys examined is specially marked in the alloy with 22 per cent. nickel—*i.e.* the least magnetic alloy—but is almost absent from the highly magnetic alloy with 49 per cent. nickel. The presence of 80 per cent. nickel is necessary to reverse the sign of the effect. A. W. Smith and R. W. Sears also investigated the Hall effect in the permalloys.

J. Hopkinson studied the **magnetic properties** of nickel-steels; he observed that a 25 per cent. nickel-steel is practically non-magnetizable at ordinary temp. when the permeability is only 1·4, and the induction, B, is proportional to the magnetizing force. This steel retained its non-magnetic condition when heated up to 700° or 800°, and it did not recalesce when cooled. The steel became ferromagnetic when it was cooled a little below 0°, and the magnetization was strongly intensified by further cooling. When the nickel-steel was cooled to −50°, and returned to 13°, it had changed from a non-magnetizable to a magnetizable substance, and it remained magnetizable even up to 580°; but if it be kept in the proximity of this temp., 580°, it again becomes non-magnetizable, and remains so when cooled to the temp. of the room. All this shows that the 25 per cent. nickel-steel can exist in two quite different states both of which are stable. At higher temp. ordinary steels exhibit similar phenomena, but to a less degree. The heat treatment which causes these remarkable changes in the magnetic permeability produces corresponding changes in other physical properties—sp. gr., tensile strength, electrical resistance, etc. The relations between the magnetic induction, B, and magnetizing force at 13°, for alloys which had been rendered ferromagnetic by cooling to about −50°, are shown in Fig. 243; and the variations of induction with temp. with magnetizing forces, H, respectively 6·7 and 64 gausses, in Figs. 244 and 245. There are marked differences in the two alloys. The addition of small

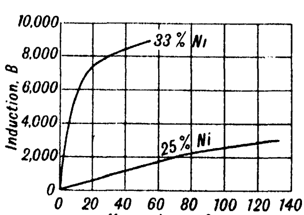
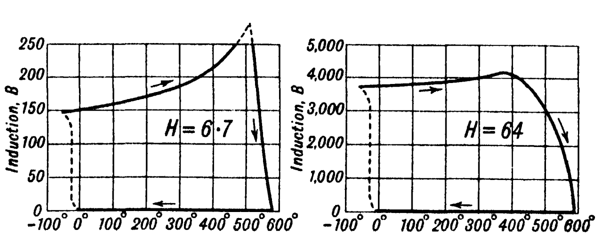


FIG. 243.—Magnetic Induction of Nickel-Steels at 13°.



FIGS. 244 and 245.—Variation of Magnetic Induction with Temperature of a 25 per cent. Nickel-Steel with Different Magnetizing Forces.

amounts of nickel to iron increases the magnitude of the irreversible anomaly until a maximum is reached with about 25 per cent. of nickel. Further additions of nickel greatly reduce the anomaly by lowering the temp. at which the ferromagnetism disappears on heating, and raising the temp. at which it appears on cooling, until both closely approach one another at about 200°. As shown in Fig. 246, the 33 per cent. alloy is practically reversible when the magnetizing force is raised to 30·3 gausses. With a 73 per cent. nickel-steel, no material

difference was observed between the critical temp. for heating and cooling. Hence, added J. Hopkinson, it is curious to remark that the magnetic induction for considerable forces is greater than in steel with 33 per cent. nickel, and that it is greater than for an equivalent mixture of iron and nickel, however the particles might be arranged in relation to each other. Observations were also made by N. S. Akuloff, A. M. Armour, O. von Auwers and co-workers, S. J. Barnett, D. Binnie, O. E. Buckley, E. C. Bullard, P. P. Cioffi, E. Czerlinsky, O. Dahl and J. Pfaffenberger, E. M. Deloraine, H. A. Dickie, M. Fischel, D. C. Gall, F. L. Garrison, P. Goerens, W. T. Griffiths, B. Hague, S. Kaya and A. Kussmann, A. Kussmann and B. Scharnoff, F. Lichtenberger, M. Medici, H. Nakamura, P. Nicolau, J. H. Partridge, V. Retzow, J. L. Snoek, T. Spooner, F. Stäblein, R. L. Steinberger, K. Takahashi, E. M. Terry, H. Tomlinson, L. Tonks and K. J. Sixtus, H. Tscherning, F. Tyler, P. Weiss, L. W. Wild, J. Würschmidt, and T. D. Yensen. R. Gans found permalloy can be diamagnetic in fields of 8000 gauss. C. Biéler-Butticaz studied the effect of cold-work on the magnetic properties of invar.

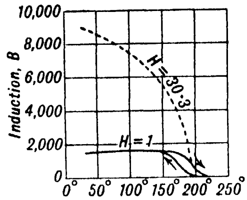


FIG. 246.—Variations of Magnetic Induction with Temperature for a 33 per cent. Nickel-Steel with Magnetizing Forces of 1·0 and 30·3 gausses.

H. Masumoto measured the intensity of magnetization of the iron-nickel alloys, and the results are summarized in Fig. 247, where F denotes ferrite; M, martensite; and A, austenite. The magnetization curve of the reversible alloys has a form similar to that of iron or nickel, but the irreversible alloys are less magnetizable. There is a marked minimum in the curve at 30 per cent. nickel, and maxima at 5 and 45 per cent. nickel. The subject was discussed by T. Kase, K. Honda, G. W. Elmen, W. T. Griffiths, F. Hegg, A. Schulze, E. Gumlich and co-workers, H. Kühlewein, and R. E. Reinhart. C. F. Burgess and J. Aston measured the magnetization curves of a series of iron-nickel alloys with magnetizing forces between H=10 and 100. The extremes are indicated in Table XVII. The hysteresis curves of electrolytic iron (dotted) and of a 47·08 per cent. nickel alloy (continuous) are given in Fig. 249. The coercive force (for $H_{\text{max.}}=200$) and retentivity (for $H_{\text{max.}}=200$) are given in Table XVIII. H. D. Arnold and G. W. Elmen's values for the initial permeability, B/H, of iron-nickel alloys—cooled slowly from about 900°, reheated to 600°, and then quickly cooled by removal from the furnace and laid on a copper plate at room temp.—are shown in Fig. 248. The maximum occurs with the alloy containing 78·5 per cent. of nickel, the so-called permalloy. R. M. Bozorth value for the hysteresis loop of hard-drawn permalloy (Ni : Fe=81 : 19) is shown by the continuous curve, Fig. 250, and of the annealed by the dotted curve, Fig. 250. The corresponding Barkhausen effects, dB/dH, for the hard-drawn wire and the annealed wire are shown in Fig. 251; $dH/dt=0·047$ gauss per second. The effect was studied by H. Barkhausen, B. van der Pol, W. Gerlach, W. Gerlach and P. Lertes, K. Zschiesche, P. Weiss and G. Ribaud, G. J. Sizoo, S. R. Williams, J. F. Dillinger, E. P. T. Tyndall, E. P. T. Tyndall and J. M. B. Kellogg, S. Procopiu,

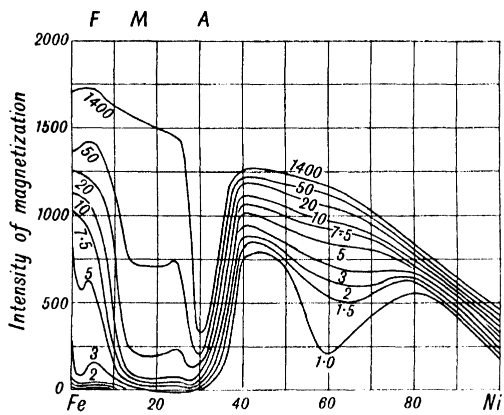


FIG. 247.—The Intensity of Magnetization of the Nickel-Iron Alloys.

TABLE XVII.—MAGNETIC INDUCTION OF IRON-NICKEL ALLOYS.

Nickel (per cent.)	H = 10				H = 100			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched at 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched at 900°
0·27	2,600	6,000	9,100	10,450	17,900	18,400	18,300	18,100
0·56	5,900	5,100	11,950	12,000	18,200	18,500	18,400	18,400
1·07	3,500	5,100	11,500	7,600	17,800	18,250	18,400	18,400
1·93	4,850	6,600	10,600	9,700	18,300	18,550	18,400	18,400
7·05	4,850	10,000	9,500	9,300	17,250	19,250	18,750	18,500
8·17	2,600	5,100	8,000	8,350	17,250	17,350	18,300	18,500
10·20	50	1,450	5,300	7,950	13,800	12,850	18,350	18,600
11·29	150	2,800	4,100	5,600	13,950	16,000	15,400	18,050
12·07	350	750	2,700	4,600	13,450	12,200	13,850	17,700
13·11	100	450	700	2,450	12,600	6,650	11,550	16,650
19·21	400	400	650	2,200	12,050	10,350	12,050	17,200
22·11	100	100	400	300	6,800	4,500	8,500	8,050
25·20	0	0	50	50	0	100	1,050	850
26·40	0	0	100	0	0	0	1,200	850
28·42	0	0	0	0	0	100	100	100
35·09	4,850	6,400	8,800	6,500	11,850	11,700	12,300	11,800
47·08	7,850	10,600	13,650	10,300	16,000	16,200	16,500	16,000
75·06	8,300	7,200	8,450	8,700	11,800	11,950	12,300	12,100

TABLE XVIII.—THE COERCIVE FORCE AND RETENTIVITY OF IRON-NICKEL ALLOYS.

Nickel (per cent.)	Coercive force				Retentivity			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched at 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched at 900°
0·27	13·4	9·0	6·0	4·3	12,400	12,500	10,600	10,900
0·56	11·0	9·1	4·0	4·2	11,400	12,300	10,100	10,700
1·07	11·4	9·3	4·9	6·0	12,600	12,800	11,300	8,900
1·93	10·2	9·0	5·0	6·0	12,800	14,000	11,300	11,700
7·05	11·0	7·5	5·8	5·5	9,100	14,200	10,100	10,700
8·17	12·5	10·0	6·3	6·0	8,000	12,500	9,600	9,500
10·20	44·0	18·0	8·7	7·2	8,700	9,500	8,600	10,300
11·29	32·5	13·5	9·2	8·8	9,200	11,800	7,000	9,500
12·07	35·0	35·5	10·7	9·5	8,800	9,800	5,900	9,500
13·11	34·8	32·5	31·5	14·9	8,500	4,500	7,700	11,900
19·21	38·5	40·5	34·2	15·5	8,400	8,300	8,500	9,300
22·11	44·5	51·8	37·0	42·7	5,000	3,900	6,300	6,100
25·20	Non.	200+	50·3	64·5	Non.	200	1,000	1,000
26·40	Non.	200+	45·5	66·3	Non.	200	1,100	900
28·42	Non.	200+	200+	200+	Non.	2,000	400	400
35·09	7·9	6·5	1·9	2·7	4,800	6,200	4,000	4,500
47·08	6·7	5·5	1·6	1·9	7,700	9,000	8,700	5,200
75·06	3·1	3·5	1·9	1·5	6,000	4,600	3,600	4,200

and L. Pfaffenberger—*vide* iron. W. Neumann, E. P. Harrison and co-workers, and E. M. Guyer studied the effect of high-frequency electromagnetic fields on the permeability; R. Goldschmidt, the relation between permeability and hysteresis; O. Dahl and J. Pfaffenberger, the anisotropic effect; D. S. Steinberg, the reversal wave of magnetization; and H. Kühlewein, the magnetic after-effect.

A. E. Kennelly discussed the magnetic reluctivity, *i.e.* the inverse of the magnetic permeability, $\mu-1$, of permalloy. S. W. J. Smith observed the changes

in the magnetic permeability with temp. between 0° and 850°, and attempted to explain the results in terms of the theory of solid soln., and the constitution of meteorites. For G. W. Elmen's observations, *vide supra*, Figs. 243 to 245. Alloys with permeabilities higher than iron were also studied by J. Würschmidt, F. Hegg, K. Honda, A. M. Portevin and co-workers, and K. Zschiesche. T. D. Yensen found for purified iron, and 50 and 78 per cent. nickel alloys, the respective values: Initial permeability 700, 3000, and 5850; maximum permeability, 26,000, 70,000,

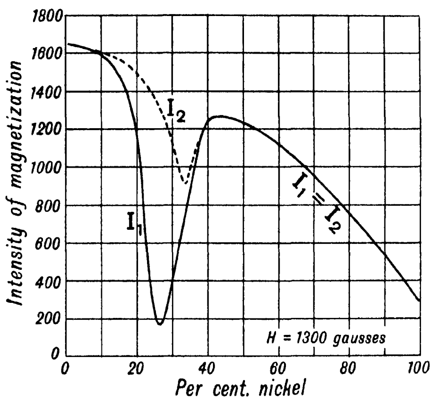


FIG. 248.—The Intensity of Magnetization of Nickel-Steel.

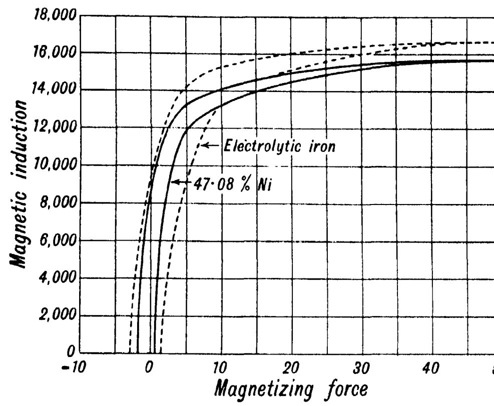


FIG. 249.—Hysteresis Curves of Iron and of an Iron-Nickel Alloy.

and 74,000; saturation value, 22,600, 15,500, and 10,500; hysteresis loss, 600, 220, and 200 ergs per c.c. per cycle for $B=10,000$; reluctivity, 8600, 7300, and 5500 gausses; coercive force, 0·20, 0·05, and 0·05 gilberts per cm.; electrical resistance, 10, 46, and 21 microhms at 20°; and sp. gr., 7·9, 8·3, and 8·6. The reluctivity curve of permalloy was measured by A. E. Kennelly and found to have two branches, $(9{\cdot}5-225H)10^{-5}$, and $(0{\cdot}5+9{\cdot}8H)10^{-5}$, with a minimum reluctivity of $1{\cdot}15\times10^{-5}$ oersted-cm., for $H=0{\cdot}06$ gilberts per sq. cm. The magnetic

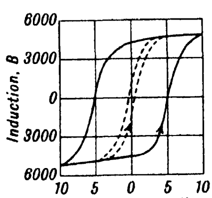


FIG. 250. — Hysteresis Loops of Hard-drawn (continuous) and Annealed (dotted) Permalloy.

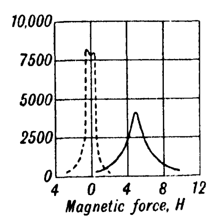


FIG. 251.—Barkhausen Data for Hard-drawn (continuous) and Annealed (dotted) Permalloy.

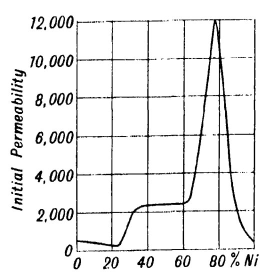


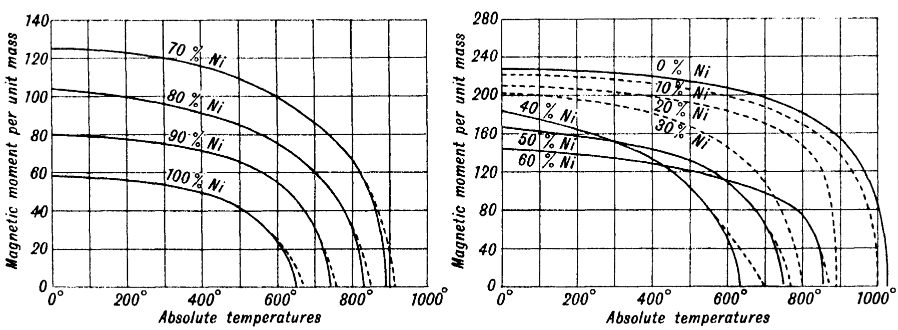
FIG. 252.—The Magnetic Permeability of the Iron-Nickel Alloys.

properties of iron-nickel alloys were discussed by W. E. Williams, E. Colver-Glauert and S. Hilpert, K. J. Sixtus and L. Tonks, E. Gerold, S. S. Sidhu, W. F. Barrett, C. E. Guillaume, R. Paillot, M. Peschard, H. Neumann, F. Preisach, J. Trowbridge and S. Sheldon, K. Honda and K. Kido, K. Honda and S. Shimizu, A. Schulze, H. D. Arnold and G. W. Elmen, L. W. McKeehan, D. Binnie, M. Peschard, D. Foster, R. Glocker and co-workers, F. Pölzguter, O. Veletztaja, and F. Sauerwald. W. Kohl found for the saturation values, $4\pi I$, of steel with

20 per cent. nickel in magnetic fields of H c.g.s. units heated to 1300°, quenched, and then heated 3 to 5 hrs. to θ°, and then quenched.

	H	50	100	200	400	800
$4\pi I$	1300° and quenched	6,640	11,290	15,140	18,200	19,730
	Cooled 30 min. in liquid air	6,245	11,030	15,010	18,000	19,260
	350° and quenched	9,830	14,610	17,740	19,400	19,860
	500° and quenched	4,280	16,470	17,930	18,660	19,260
	600° and quenched	4,385	10,230	14,550	17,000	18,330
	700° and quenched	4,715	10,290	14,480	17,070	18,130
	800° and quenched	5,180	10,360	14,680	17,200	18,400
	900° and quenched	5,315	10,160	14,350	17,140	18,270
	1000° and quenched	5,845	10,830	14,820	17,910	19,070
	1150° and quenched	6,370	10,960	15,140	18,270	19,130
	1250° and quenched	6,640	11,230	15,280	18,830	19,260

C. E. Guillaume showed that the temp., θ°, at which the ferromagnetism disappears—the so-called Curie point, or critical point—in reversible steels containing 28 to 40 per cent. of nickel can be approximately represented by $\theta=34\cdot1(\mathrm{Ni}-26\cdot7)-0\cdot80(\mathrm{Ni}-26\cdot7)^2$, where Ni denotes the percentage of nickel. The subject was discussed by M. Déprez, P. Weiss, J. G. Gray, E. Colver-Glauert and S. Hilpert, and H. K. Onnes and co-workers. E. Dumont observed that between −80° and 250°, and with H varying from 14 to 50 gauss, annealed alloys with 30 up to at least 44 per cent. nickel have induction-temp. curves resembling that of Fig. 56 for $H=30\cdot3$; they gradually lose their magnetization on heating, and at the same number of degrees of temp. below the critical temp., all reversible alloys have the



FIGS. 253 and 254.—Variation of the Magnetic Moment per Unit Mass with the Absolute Temperature of Iron-Nickel Alloys.

same permeability. The permeability at any given temp. increases with the proportion of nickel; but the permeability of unannealed reversible alloys containing 39·4 to 44 per cent. of nickel, remains constant between 20° and 250°.

It may be observed that the magnetic induction, B, or intensity of magnetization, I, is regarded as being produced by a magnetizing force, H. The magnetic moment per unit vol. v_2 is $I=\mathfrak{M}/v$, but P. Weiss considered it more convenient to use the magnetic moment per unit mass, m, or $\sigma=\mathfrak{M}/m$. If the density is D, then $\sigma=l/D$, and $B=H+4\pi\sigma D$, N. J. Gebert found that with nickel-steels, quenched and tempered at various temp. followed by air-cooling, the residual magnetic induction in both steels increased considerably after tempering at 425° and over. R. L. Dowdell observed a similar rise in the residual induction after tempering to 400° or 500° in steels not subject to temper brittleness. Observations were also made by C. W. Burrows and F. P. Fahy, C. Nusbaum, and E. Colver-Glauert and S. Hilpert. For paramagnetic bodies, the susceptibility per unit mass, χ, is for many substances approximately proportional to the absolute temp., I, over wide intervals of temp. The constant $C=\chi T$ is known as *Curie's constant*. If $K=l/H=\mathfrak{M}/vH$ is the susceptibility in terms of the magnetic moment per unit vol., then $\chi=\sigma/H=K/D$.

F. Hegg measured the magnetic properties of small ellipsoids of iron-nickel alloys using magnetizing forces up to and beyond 10,000 gauss. The curves, Figs. 253 to 255, were obtained with 10,000 gauss, and they represent the

magnetic moment per unit mass as a function of the absolute temp.; and Fig. 254, for a 50 per cent. nickel alloy, shows how the intensity of magnetization changes with the magnetizing force at a number of different temp. Figs. 253 to 255 explain themselves. For the irreversible alloys, Fig. 255, the copper curves *A, B, C* show the successive values of the magnetization on warming, and they are analogous to the curves for iron and the reversible alloys in that the disappearance of magnetism occurs gradually, and appears to be independent of time. Near *C* the curves commence to drop rapidly, the reversibility disappears, and the state of the alloy is a function not only of the temp., and of the magnetizing force, but also of time which plays a preponderating *rôle*. If the heating be continued, the material loses its last traces of ferromagnetism at the transformation point on heating, θ_c. During cooling, the material retains its paramagnetic properties until the transformation point on cooling, θ_f, is passed, after which ferromagnetism appears with great rapidity. If the temp. be low enough for the return of the intensity of magnetization to the value it had before heating, the cycle will be

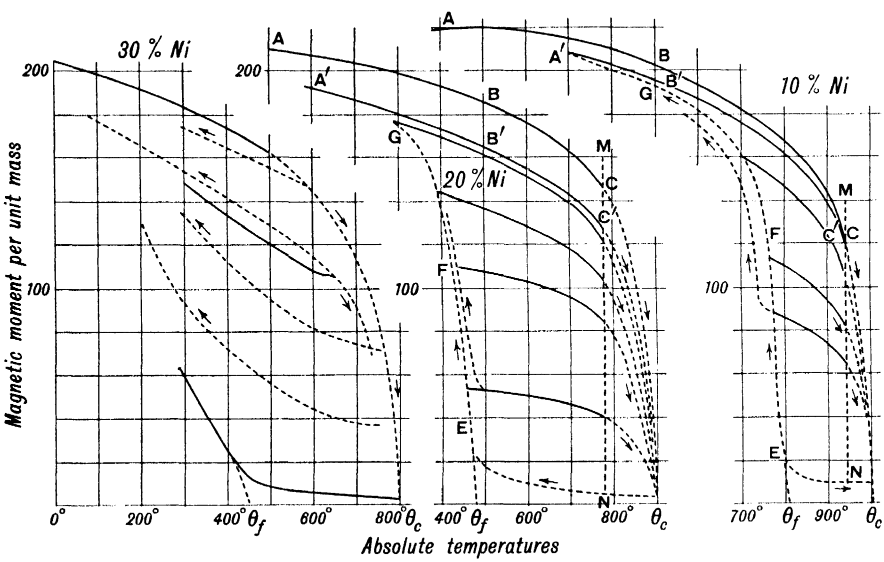


FIG. 255.—Variation of the Magnetic Moment per Unit Mass with the Absolute Temperature of Iron-Nickel Alloys.

closed. The treatment can be repeated as desired. While the first portions, *A, B, C,* of the heating curves are very little influenced by time, and can be regarded as reversible during a series of experiments, the rapidly descending portions of the curves to the right of the lines *MN*, Fig. 255, can be perceptibly modified by increasing the rapidity of the variation of temp. The nearer the temp. is to θ_c, and the longer it is held thus, the more advanced is the transformation. The return of the ferromagnetism on cooling is characterized by a still greater instability. The curves, *E, F, G,* are not reversible, and it is difficult to obtain the same values a second time. If on reaching any point, *E, F, G,* the heating is resumed, the alloy will pass through a new cycle, similar to the one just described in all respects excepting size. The nearer to θ_c, the point at which reheating begins, the smaller will it be. Amongst the properties common to all the curves, *A, B, C, A′, B′, C′,* etc., the most important is then almost complete reversibility up to the region bounded by *MN*. The more rapidly the experiments are made, the less do these curves differ from those for reversible alloys. In the diagram, the reversible portions are drawn with continuous lines, and the irreversible portions with dotted lines; the arrows show the directions the different curves are traversed.

F. Hegg also observed that if lines corresponding with any two temp. are drawn parallel to the axis of the magnetic moment across the reversible curves, the ordinates for a given alloy cut off by these curves are nearly proportional. Hence it is supposed that a part of the material is in the paramagnetic state, and up to a certain temp., MN, offers such a stability that the reversibility is not altered. It is only in the region between MN and the point θ_c that the ferromagnetic material not yet transformed will undergo, at constant temp., partial or complete transformation to any great extent. If, however, the alloy is maintained at a sufficiently low temp., the excess of paramagnetic material will very gradually be transformed into the ferromagnetic state. Thus, the alloy with 30 per cent. nickel, after being heated beyond the transformation point, was measured at room temp.; and in three weeks later, the permeability had increased 5 per cent.; and the ageing of nickel-iron alloy at a low temp. increases its ferromagnetic qualities, while annealing at a temp. near the transformation point decreases them. R. Forrer, and Y. Dorfman studied the magnetic moment of the alloys; T. Nishina, the demagnetization of nickel; and P. Weiss, the residual magnetism.

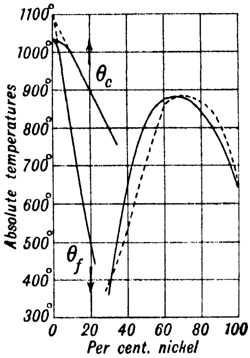
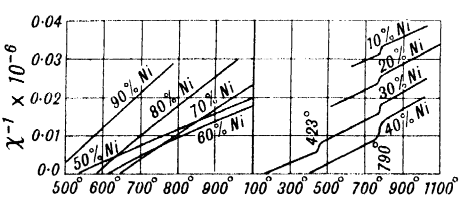


FIG. 256.—The Temperatures of Magnetic Transformation or the Curie Points of the Iron-Nickel Alloys.

The magnetic transformation temp. θ, or Curie points, for the iron-nickel alloys were observed by F. Osmond, and L. Dumas magnetically, by W. Guertler and G. Tammann with time-temperature curves, by O. Boudouard thermoelectrically, and by R. Ruer and E. Schüz thermally. F. Hegg's results are shown in Fig. 256. The transformation points θ_c and θ_f for irreversible alloys lie on two straight lines which, if produced, intersect on the line corresponding with pure iron, where $\theta_c=\theta_f=820°$ C. or 1093 K.—actually, for purified iron, the observed temp. is 758° C. or 1031° K. Some discrepancies are due to the effects of traces of impurity—carbon, manganese, etc.—on the critical points. P. Weiss, working with F. Hegg's alloys, found that the two magnetic constants which are characteristic for homogeneous solid soln. of ferromagnetic bodies are σ_0, the saturation value of the magnetic moment per unit mass at the absolute zero of temp., and C, Curie's constant (*vide supra*). P. Weiss deduced the relation $C=\chi(T-\theta)$, where θ here denotes the Curie transformation point, and T, the temp. of observation. Here C is the Curie constant which the substance would have if it were to become paramagnetic by the suppression of intermolecular reactions. In many cases, the linear variation of the reciprocal of the magnetic susceptibility, χ^{-1}, with temp., has been observed, and P. Weiss has also shown that in the case of homogeneous solid soln., both σ_0 and C vary as linear functions of the composition. Curie's law, however, is not generally true, and never exactly true. Figs. 257 and 258 by P. Weiss and G. Foëx show the values of χ^{-1} as functions of the temp. Each alloy with over 40 per cent. of nickel furnished a straight line from which both θ and C could be determined by means of the relation $\chi^{-1}=(T-\theta)/C$. On cooling the 40 per cent. nickel alloy from a high temp., χ^{-1} at first followed a straight line with a Curie constant of 0·0256, and other measurements with increasing temp., except for a small and constant deviation, due to an error of observation,



FIGS. 257 and 258.—Reciprocals of the Magnetic Susceptibilities per Unit Mass as Functions on the Temperature of Iron-Nickel Alloys.

followed the same line, so that the first portion of the curve is reversible. The Curie point corresponding with this is nearly $\theta=423°$ or 696° K., and $C=0{\cdot}0251$. On cooling from 790° to 730°, a transformation occurs, which follows another straight line for which $\theta=335°$ or 608° K. The phenomenon is irreversible below 730°. On heating, the points fall below those obtained on cooling, and the heating curve approaches the cooling curve as 730° is approached. The phenomenon is complicated by its dependence on time in the irreversible region. The alloy is still reversible in the transformation region. A third line was observed, not represented in the diagram, for which $\theta=300°$ or 573° K., and $C=0{\cdot}091$. The alloys with 10, 20, and 30 per cent. nickel resembled in many respects the 40 per cent. alloy. All showed the same irreversibilities and the same type of transformation at about 790°, and all gave several Curie temperatures, and Curie constants corresponding with restricted temp. intervals. The lower dotted line in Fig. 259 represents the Curie constants, C, obtained by P. Weiss and G. Foëx. The upper curve gives F. Hegg's values of σ_0, the magnetic moment per unit mass at saturation, obtained by extrapolation to absolute zero. The results for C and σ_0 agree with the existence of a compound Fe_2Ni. P. Weiss and G. Foëx said: The iron-nickel alloys form two uninterrupted series of solid soln., the first between Fe and Fe_2Ni, and the second between Fe_2Ni and Ni. The location of Fe_2Ni is also associated with the transition region from irreversible to reversible nickel-iron alloys as shown in Fig. 176. L. H. Adams and J. W. Green observed that pressure has no effect on the critical temp. A. Schulze gave the results in Fig. 260 for the saturation values, $4\pi I_\infty$, of the iron-nickel alloys.

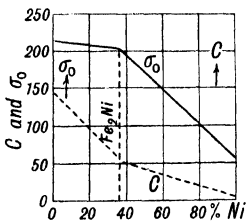


FIG. 259.—The Curie Constants and Saturation Magnetic Moments of Iron-Nickel Alloys.

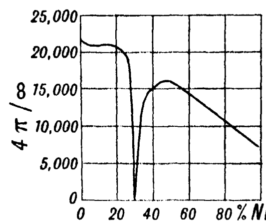


FIG. 260.—The Saturation Value of the Iron-Nickel Alloys.

H. Nagaoka and K. Honda, K. Honda and K. Kido, and K. Honda and S. Shimizu studied the **magnetostriction** effect in steels with 24 to 70 per cent. of nickel. For 28·74 per cent. nickel steel, the change in length $\delta l/l\times10^6$ is $-0{\cdot}01$ for $H=0{\cdot}2$, and 4·67 for $H=404$ with a load in tension of 1427 grms. per sq. mm., and $-0{\cdot}02$ for $H=0{\cdot}5$, and 3·92 for $H=405$ for a load of 4856 grms. per sq. mm. With 50·72 per cent. nickel-steel, $\delta l/l\times10^6$ is $-0{\cdot}09$ for $H=0{\cdot}2$, and 14·20 for $H=390$ for a load of 890 grms. per sq. mm., and $-0{\cdot}01$ for $H=0{\cdot}2$, and $-1{\cdot}14$ for $H=388$ when the load is 6652 grms. per sq. mm. With 70·32 per cent. nickel-steel, $\delta l/l\times10^6$ is $-0{\cdot}18$ for $H=0{\cdot}3$ and 8·35 for $H=391$ when the tension load is 806 grms. per sq. mm., and $-0{\cdot}01$ for $H=0{\cdot}2$ and 1·24 for $H=391$ when the load is 5686 grms. per sq. mm. A. Schulze's results for the effect of the field strength on the magnetostriction are plotted in Fig. 261. Observations on the magnetostriction were also made by L. W. McKeehan and co-workers, F. D. Smith,

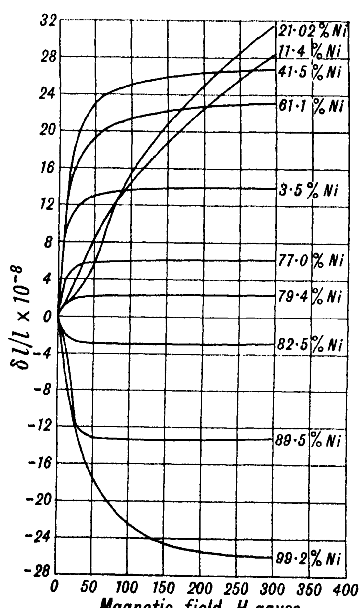


FIG. 261.—The Effect of the Magnetic Field on Magnetostriction.

Y. Masiyama, O. von Auwers, H. Masumoto and S. Nara, E. Gumlich and co-workers, and W. Steinhaus. By the combined effect of magnetic and thermal treatment between $-75°$ and $300°$, A. W. Gray and co-workers obtained a permanent increase in 35·25 per cent. nickel-steel of 55 microns per metre at room temp. J. S. Rankin studied the effect of overstrain on magnetostriction.

K. Honda and co-workers found that in all cases, longitudinal magnetization produced an increase in length—*Joule effect*; and reciprocally, mechanical elongation produced an increase of magnetization. The elongation was greater with a specimen after annealing than when in the hard-drawn state. The elongation produced by magnetization under tension was reduced, and in some cases even changed to a contraction by increasing the load. The effect of cooling on the magnetic elongation was similar to its effect on the intensity of magnetization. With steels containing over 28·7 per cent. of nickel, and cooled in liquid air, the elongation was diminished in weak magnetic fields and increased in strong fields; with steels containing less nickel, the initial elongation vanished. The ratio of the elongation in liquid air to that at ordinary temp. increased in strong fields with a decrease in the content of nickel. With a magnetizing force of 500 gauss, the ratio amounted to 1·6 with 86 per cent. of nickel; 3·7 with 28 per cent.; and 100 with 24 per cent. The elongations before and after cooling reversible nickel-steels were the same, but the elongations of reversible steels were always greater after cooling. A 25 per cent. nickel-steel did not elongate appreciably at ordinary temp. or at the temp. of liquid air. The changes in length by fields as weak as that of the earth were generally smaller than 10^{-7}. The increases in vol. of magnetized ellipsoids are practically proportional to the magnetizing forces. The effect with alloys of small thermal expansivity is greater than that occurring with any other known ferromagnetic substance. The torsion produced in nickel-steels by the combined action of longitudinal and circular magnetic fields—the *Wiedemann effect*—is smaller than that observed in the case of iron. L. W. McKeehan thought that the peculiar magnetic properties of permalloy might be due to the nearly perfect compensation in a group containing one iron atom and four nickel atoms of the magnetostrictions characteristic of the pure metals.

K. Honda and T. Tanaka measured the effect of magnetization on the elastic modulus, E, and the coeff. of rigidity, K, of the iron-nickel alloys. The results are summarized in Figs. 262 and 263. The elastic constants are in all cases

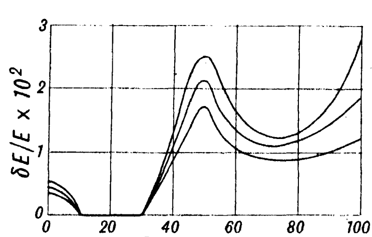


FIG. 262.—The Effect of Magnetization on the Elastic Modulus of Iron-Nickel Alloys.

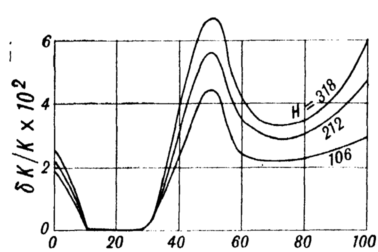


FIG. 263.—The Effect of Magnetization on the Rigidity of Iron-Nickel Alloys.

increased by magnetization for all fields except with the so-called irreversible steels in which a small decrease occurs. The change in the modulus of rigidity is about three times greater in the case of carbon steels, cobalt-iron, and nickel-iron alloys. K. Honda and T. Terada stated that the change in coeff. of elasticity with change of magnetization is generally small. With 28·74 per cent. nickel, the change in elasticity $\delta E/E \times 10^2$ is 0·07 for $H=41$, and 0·48 for $H=391$ for a load of 1247 grms. per sq. mm., and 0·03 for $H=6·2$ and 0 for $H=418$ with a load of 4·70 grms. per sq. mm. With 50·72 per cent. nickel-steel, the change is 0·09

for $H=0{\cdot}8$, and 8·65 for $H=388$ when the load is 890 grms. per sq. mm., and 0 for $H=1{\cdot}8$, and 1·13 for $H=387$ when the load is 5003 grms. per sq. mm. With 70·32 per cent. nickel-steel, $\delta E/E\times 10^2$ is $-0{\cdot}14$ when $H=0{\cdot}7$, and 4·92 when $H=386$ for a load of 806 grms. per sq. mm., and $-0{\cdot}01$ for $H=0{\cdot}6$ and 0·70 for $H=393$ when the load is 4882 grms. per sq. mm. The change in the coeff. of rigidity $\delta K/K\times 10^2$ for 28·74 per cent. nickel-steel is 0·29 for $H=12{\cdot}2$, and 0·48 for $H=409$ with a load of 928 grms. per sq. mm., and 0·06 for $H=6{\cdot}2$ and 0·38 for $H=403$ for a load of 4096 grms. per sq. mm. With 50·72 per cent. nickel, $\delta K/K\times 10^2$ is $-0{\cdot}60$ when $H=4{\cdot}0$, and 7·16 when $H=387$ for a load of 1114 grms. per sq. mm., and $-0{\cdot}22$ for $H=3{\cdot}8$, and 3·60 for $H=394$ when the load is 8725 grms. per sq. mm. With 70·32 per cent. nickel, $\delta K/K\times 10^2$ is $-1{\cdot}18$ when $H=3{\cdot}3$, and 6·55 when $H=394$ for a load of 1086 grms. per sq. mm., and $-0{\cdot}60$ when $H=2{\cdot}3$ and 2·08 for $H=414$ when the load is 8510 grms. per sq. mm. The change with Poisson's ratio $\delta\sigma/\sigma\times 10^2$ is $-1{\cdot}0$ for $H=20$, and $-1{\cdot}1$ for $H=300$ for a load of 1770 grms. per sq. mm. with 28·74 per cent. nickel-steel; $-0{\cdot}3$ for $H=10$ and $-11{\cdot}1$ for $H=350$ for a load of 3350 grms. per sq. mm. for 50·72 per cent. nickel; and $-1{\cdot}6$ for $H=10$, and $-13{\cdot}8$ for $H=300$ for a load of 3280 grms. per sq. mm. on 70·32 per cent. nickel-steel. Observations were made by H. Tomlinson, T. Aizawa and G. Wachi, K. Nakamura, and H. Nagaoka and K. Honda on the effect of stress on the magnetization of nickel-steels. K. Honda and T. Terada found that the change of magnetization δI_i with initial loading, and δI_c with cyclic loading for loads in tension, I grms. per sq. mm., for steel with 28·74 per cent. of nickel, is:

	I	1370	2706	4077	6818
$H=0{\cdot}45$	δI_i	20·1	62·4	97·2	130·3
	δI_c	26·4	57·5	77·6	94·1
$H=374{\cdot}3$	δI_i	1·4	—	4·0	6·6
	δI_c	1·3	—	3·9	6·6

and with 50·72 per cent. of nickel:

	I	1645	3249	4894	6540	8185
$H=0{\cdot}29$	δI_i	103·3	322·6	277·8	300·3	311·1
	δI_c	91·1	138·8	153·2	155·1	153·7
$H=360$	δI_i	0	0	0	0	0
	δI_c	0	0	0	0	0

The changes of magnetization under constant tension by twist, and by the combined effect of tension and twist, were also examined. In all cases the reciprocal nature of the changes of strains by magnetization and of the changes of magnetization by strain were established. For instance, magnetic elongation under constant tension and of magnetization under constant tension; of elongation by tension under a constant field, and the change of magnetization by tension under a constant field; of magnetic twisting under a constant couple, and magnetization under a constant twist; and of the change of rigidity under a constant field, and the change of magnetization by twist under a constant field. K. Honda and T. Tanaka observed that the elastic constants of the nickel-iron alloys are increased in a magnetic field; and S. R. Williams, W. del Regno, and G. Guzzoni and D. Fuggiani, the relation between the magnetic and mechanical properties. A. W. Smith and J. Dillinger observed that in permalloy with less than 81 per cent. nickel, a tensile stress increases the intensity of magnetization for low magnetic fields, but decreases the magnetostrictive expansion and the change in the thermoelectric force; but with over 81 per cent. of nickel, tension decreases the intensity of magnetization for low magnetic fields, but increases the magnetostrictive contraction and change of thermoelectric force. F. D. Smith studied the effect for alternating current with 40 per cent. nickel alloys; and S. J. Barnett, the gyromagnetic rotation of permalloy.

G. Belloc studied the absorption of furnace gases by nickel-steel. With 50 grms. of wire extracted at different temp., the vol. v c.c., and the percentage composition of the gas by vol., was :

	350°	440°	610°	640°	740°	820°	950°
Total vol., v	0·95	1·38	3·70	2·14	2·70	2·35	11·20
Carbon dioxide	37	14	8	0	0	0	0
Carbon monoxide	40	26	49	50	49	56	67
Hydrogen	23	60	39	44	47	40·8	28·5
Nitrogen	0	0	4	6	4	2·2	4·5

H. C. H. Carpenter attributed the brittleness of nickel wires used as resistance wires in electric furnaces to the recrystallization of the metal, and to the penetration of gases. The subject was discussed by W. Fröhlich. H. Remy and H. Gönningen studied the catalysis of the $2H_2+O_2$ reaction by the alloy. In 1807, A. and C. R. Aikin observed that meteoric iron is " scarcely at all oxydable by exposure to the weather," and added that " it is highly probable therefore that nickel may become a metal of vast importance if its power of protecting iron from rust be fully established." T. Fleitmann noticed that the nickel-iron alloys offer a much greater resistance to the corroding influence of the atmosphere than does iron alone. The subject was studied by F. A. Fahrenwald, L. Losana and G. Reggiani, B. Bogitch, H. T. Kalmus and K. B. Blake, H. G. Haase, W. H. Creutzfeldt, H. J. French and co-workers, W. Ackermann, R. Mallet, and R. W. Bailey and A. M. Roberts. L. B. Pfeil observed that a three-layer scale is formed when nickel-iron, or nickel-steel is heated at 1000° in air for several hours. With nickel-iron, very little nickel occurred in the outer layer, but a remarkable enrichment of nickel as metal was found on the innermost layer, and no nickel was found in the outer layer of nickel-steel where the outer layer formed one-seventh of the whole scale. The middle layer—one-half the whole scale—with nickel-steel contained only traces of nickel ; whilst the innermost layer contained 2·5 times as much nickel as the original steel. L. B. Pfeil said : Under the microscope, the cross-section of the scale showed important differences from the scale derived from plain iron or iron-carbon steels : (i) The inner layer contained minute, metallic particles embedded in oxide ; (ii) intercrystalline penetration in the core was more pronounced ; (iii) beyond the range of intercrystalline oxidation of the core, an altered zone is present in the metal. In this zone, there are present an enormous number of extremely minute specks, probably iron oxide. G. Tammann and G. Siebel studied the temper colours of the iron-nickel alloys. J. Riley said that alloys with over 25 per cent. of nickel are practically free from rusting, and that while 5 per cent. of nickel reduces the corrosion of iron in acid in the ratio 100 : 83, 25 per cent. of nickel reduces the corrosion in the ratio 100 : 1·15. R. A. Hadfield found that the percentage loss by the corrosion of forged steel containing 0·13 per cent. of carbon and

Nickel	0·93	3·82	7·62	11·39	29·07 per cent.
Loss	3·23	2·95	2·77	2·60	1·34 ,,

and H. C. H. Carpenter and co-workers observed that with steel containing 0·40 to 0·52 per cent. of carbon, and 0·75 to 1·03 per cent. of manganese, the losses by corrosion after 32 days' exposure in water ; after 33 days in sea-water ; and after 17 days in 50 per cent. sulphuric acid, were :

Nickel		0	1·20	2·15	4·25	6·42	12·22	15·98	19·91 per cent.
Loss	Water	0·15	0·11	0·10	0·11	0·12	0·10	0·09	0·09 ,,
	Sea-water	—	0·23	0·26	0·26	0·23	0·23	0·18	0·14 ,,
	Acid	0·80	1·10	0·72	0·71	0·58	0·44	0·28	0·28 ,,

C. F. Burgess and J. Aston exposed plates of nickel-iron alloys to the weather for 162 days from July to February, and observed the loss estimated in kgrms. per sq. metre per year ; and also to the action of 20 per cent. sulphuric acid for an

hour, and estimated the loss in grms. per sq. dm. per hour. The following is a selection from their results :

Ni	.	0·270	1·070	10·200	19·210	25·200	35·090	47·080	75·660 per cent.
Air	.	0·6330	0·5070	0·0910	0·0720	0·0540	0·1830	0·1600	0·0490 ,,
Acid	.	0·288	0·283	0·132	0·088	0·112	0·088	0·062	0·0215 ,,

J. G. Eaton stated that up to 2 per cent. of nickel exerted no protective action on steel, 3 to 4 per cent. reduced the corrosion in the ratio 100 : 95 ; E. Crowe found that 2·6 to 2·9 per cent. of nickel reduced the corrosion ratio from 100 to 98 ; H. A. Wiggin observed that the introduction of about 3 per cent. of nickel reduces the corrodibility of steel by salt-water, and by steam nearly one-half. J. Davis also noted that nickel increases the resistance of steel wires to corrosion. H. M. Howe found that 3·03 per cent. of nickel reduced the corrosion in neutral or faintly acid soln. in the ratio 100 : 77, and 26 per cent. of nickel in the ratio 100 : 31 ; whilst H. Wiggin found that 3·03 per cent. of nickel reduced corrosion in the ratio 100 : 64. G. Tammann found that 10 per cent. of chromium or 0·11 molecule suffices to make the nickel alloy passive—*vide* iron-chromium alloys. C. Diegel found that the corrosion by sea-water was reduced in the ratio 100 : 65 by 6·14 per cent. nickel, and 100 : 26 by 29·7 per cent. nickel. J. A. N. Friend and co-workers found that by taking the corrosion factor with a steel containing 0·29 per cent. carbon and 0·39 per cent. manganese to be 100, in all cases, the corrosion with steels containing :

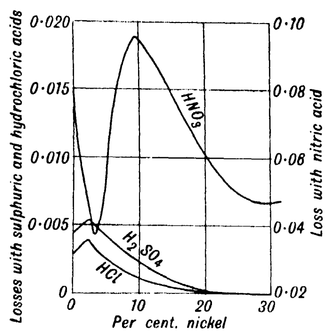


FIG. 264.—The Corrosion of Nickel-Steels by Acids.

Ni	3·72	6·14	26·24	3·4	3·5 per cent.
Cr	—	—	—	1·0	1·12 ,,
Tap-water . . .	83	69	51	77	90
Sea-water . . .	77	79	45	82	90
Alternate wet and dry .	43	36	8	47	52
0·05 per cent. H_2SO_4 .	85	82	54	87	93
0·5 per cent. H_2SO_4 .	55	63	8	132	413

T. S. Fuller studied the effect of steam on the endurance tests for nickel-steel. Y. Utida and M. Saito observed the weight of oxygen, in grams per sq. cm., taken up in oxidation when the metal is heated for an hour at 1100° ; and also the loss in weight in grams per sq. cm. in 24 hrs., and with samples of steel with 0·05 to 0·18 per cent. of carbon, immersed in 10 per cent. soln. of the different acids, they found :

Nickel .	0	8·2	23·57	42·99	60·09	81·06	98·98 per cent.
At 1100° in air	0·0212	0·0369	0·0227	0·0160	0·0077	0·0046	0·0030
HNO_3 . .	0·9380	0·5090	0·4087	0·3125	0·1050	0·0275	0·0221
HCl . .	0·0712	0·0602	0·0342	0·0028	0·0012	0·0009	0·0015
H_2SO_4 .	0·0990	0·0112	0·0037	0·0003	0·0006	0·0005	0·0006

S. Endo's results, plotted in Fig. 264, represent the losses, in grams per sq. cm., suffered in 5 hrs. by alloys with 0·45 to 0·54 per cent. of carbon, and the proportions of nickel indicated in the diagram. H. Kirscht studied the effect of nickel on the oxidation of iron ; M. Sauvageot, the action of steam ; R. Müller and co-workers, the action of molten fluorides. R. Schanzer found that cubes of 0·6 per cent. carbon-steel 140 grms. in weight, after 15 hrs.' exposure lost in weight,

	HCl (sp. gr. 1·2)	HNO_3 (sp. gr. 1·2)	H_2SO_4 (sp. gr. 1·6)
Steel alone . . .	1·001	1·016	4·17 grms.
Steel with 1·2 per cent. Ni	0·279	0·847	2·39 ,,

A. M. Fairlie found that a 5 per cent. nickel alloy resists sulphuric acid very well,

and fused hydrosulphates, but it is attacked by nitric acid. W. H. Hatfield's results for iron-nickel-carbon alloys for the loss in weight in grams per sq. cm. in 24 hrs. at 15° are indicated in Table XIX. The introduction of nickel to steel

TABLE XIX.—THE ACTION OF ACIDS ON NICKEL-STEELS.

Composition					Condition	Brinell's hardness	HCl (sp. gr. 1·180)	HNO_3 (sp. gr. 1·20)	H_2SO_4 (10 per cent.)
C	Mn	Ni	Cr	Si					
0·26	0·41	4·82	Nil	0·16	As rolled	187	0·1142	0·7388	0·0221
0·16	0·33	6·05	,,	0·41	,,	157	0·0872	0·4475	0·0072
0·30	0·31	9·02	,,	0·13	,,	276	0·1593	0·6494	0·0102
0·23	0·18	12·23	,,	0·11	,,	345	0·1939	0·7123	0·0074
0·32	0·28	14·90	,,	0·12	,,	330	0·0816	0·7026	0·0028
0·26	0·31	20·08	,,	0·12	Quenched 1000°	198	0·0838	0·6887	0·0010
0·31	0·98	24·21	,,	0·34	,,	168	0·0568	0·7532	0·0008
0·18	1·00	26·1	—	—	,,	175	0·0678	0·5914	0·0006
0·18	1·07	29·3	—	0·25	,,	186	0·0290	0·7745	0·0005
0·23	0·35	36·50	Nil	0·12	,,	157	0·0237	0·5730	0·0003
0·29	0·57	44·75	,,	0·22	,,	117	0·0329	0·5684	0·0004

increases its resistance to 10 per cent. sulphuric acid. P. Kötzschke and E. Piwowarsky observed that whilst up to 6 per cent. of nickel increases the resistance of cast iron to alkaline lye, it does not improve the acid-resisting nature of the metal. A. B. Everest and co-workers observed that the nickel-silicon cast irons which had a pearlitic, sorbitic, or martensitic ground-mass generally offered a resistance to attack by sulphuric acid inferior to that of an ordinary grey cast iron. The austenitic samples showed a marked resistance, and, with 20 to 40 per cent. of nickel, there was practically no attack with 0·5 to 20 per cent. sulphuric acid.

C. G. Fink and C. M. de Croly found that with all the iron-nickel alloys they examined, the rate of corrosion in sulphuric acid soln. at first increased rapidly with increasing acid concentration, but after reaching a maximum decreased more or less rapidly again. The results with sulphuric acid showing the corrodibility, expressed as a loss in milligrams per sq. dm. per 24 hrs., are :

	Per cent. H_2SO_4 . .	5	10	25	50	75	96
Loss	98·3 per cent. Ni	250	300	290	450	635	495
	78·5 per cent. Ni	350	680	1,050	540	160	366
	47·9 per cent. Ni	1000	1,380	910	250	100	54
	37·6 per cent. Ni	1,630	1,710	950	520	180	309
	Iron . . .	13,300	4,020	15,200	2,300	350	1,120

B. C. Banerji and N. R. Dhar observed that with the 50 : 50-alloy and 20 per cent. nitric acid, the reaction was accelerated by the presence of ferrous sulphate and ferric nitrate, but not by ferric chloride. The reaction was periodic, the periods in minutes being with the acid alone, 18, 8, 3, and 1 ; with ferrous sulphate addition, 13, 5, 4, and 2 ; and with ferric nitrate addition, 12, 7, 5, 3, and 1. The periodic action also occurred with 5, 10, 15, and 17 per cent. acid. The periodic action was not so marked with the 17 per cent. acid as with the 20 per cent. acid. Finally, for most of the alloys there was a second increase in rate of corrosion in very conc. soln. In a given soln. of sulphuric acid content below 25 per cent. the rate of corrosion of various alloys increased continuously with increasing iron content of the alloy, but in a more conc. acid soln., the alloy containing 27·9 per cent. of nickel always showed the minimum rate of corrosion. At the highest acid concentrations, all the alloys were less readily attacked than was either purified nickel or purified iron. The addition of chlorate or chromate to the sulphuric acid did not produce any passivation, but actually accelerated the corrosion. The addition of less than 4 per cent. of chromium to the alloy did not improve the

resistance to corrosion, but with nichrome, containing 12·5 per cent. of chromium, there is a much lower rate of corrosion, especially in soln. of low acid concentration. Corrosion by soln. of sodium chloride, and the effect of varying the temp. were studied. The results with sodium chloride are near those obtained by H. S. Rawdon and E. C. Groesbeck. With 5 per cent. soln., with electrolytic iron, the loss was 460·8 mgrms. per sq. cm. per 24 hrs.; with the 37·6 per cent. nickel alloy, 28·50; with 47·8 per cent. nickel, inappreciable; with 78·5 per cent. nickel, 2·46; and with 98·3 per cent. nickel, 5·18. The effect with sulphuric acid in the presence of potassium chlorate, and also chromic acid were examined. It is indeed possible to make the ferro-nickel alloys passive in neutral or slightly acidic soln. by adding chlorate or chromate ions to the soln. O. B. J. Frazer and co-workers found that the maximum in the H˙ ion concentration of the sulphuric acid is below the maximum rate of corrosion. The single potentials of iron-nickel alloys against sulphuric acid soln. of various concentrations showed that in a given soln., increasing iron content of the alloy makes it continuously baser, and for a given alloy the potential assumes increasingly base values with a decrease in the acid concentration. With pure nickel, however, an anomalous result was obtained. W. Guertler and T. Liepus, W. Guertler and W. Ackermann, A. F. Yarrow, A. M. Portevin, J. Strauss, M. Sauvageot and L. Lauprete, O. Behrens, E. Wellman, M. J. Prucha, O. Föppl and co-workers, R. A. Hadfield, W. H. Hatfield, L. Aitchison, J. A. N. Friend, S. Crosdale, A. M. Portevin, T. S. Fuller, M. Ballay, E. Blau, D. H. Browne, H. M. Howe, H. Diegel, J. E. Stead, H. T. Kalmus and K. B. Blake, O. Bauer and E. Piwowarsky, W. D. Williams, P. Chévenard, A. B. Everest and co-workers, P. D. Merica, P. Koetzschke, C. G. Fink and C. M. de Croÿ, W. Rohn, J. A. Mathews, E. Maass and W. Wiederholt, F. F. Hengstenberg, A. Brunner, A. Matagrin, and R. J. McKay studied the corrodibility of the iron-nickel alloys. P. Kötzschke and E. Piwowarsky found that the addition of up to 6 per cent. of nickel in grey cast iron has very little influence in preventing corrosion by acids and salt soln. P. Kötzschke found that with hydrochloric acid, cast iron with up to 6 per cent. of nickel has the corrosion reduced by 20 to 25 per cent.; and with acetic acid the corrodibility first increases and then decreases when increasing proportions of nickel are added to cast iron. D. Saito and H. Okawa, H. J. French and V. O. Homerberg, and B. Jones studied the nitridization of the nickel-steels; R. Vogel, the action of phosphorus; and P. R. Kosting and C. Heins, the action of phosphoric acid on the alloys. G. Belloc examined the occlusion of gas by nickel-steel. N. Hudson found that carbon monoxide will combine with nickel to form the volatile carbonyl even in steels with a small proportion of nickel present. F. H. Rhodes and co-workers studied the action of phenol; and J. G. Thompson and co-workers, the action of soln. of urea and of ammonium carbonate, and M. P. Balfe and H. Phillips, tan liquors. W. E. Dennison observed the effect of coal gas condensate on the corrosion of monel metal. E. H. Schulz and W. Jenge found steel with 19·5 per cent. of nickel was attacked more than cast iron by 1 per cent. nitric acid; and J. G. Thompson found that nickel reduces the resistance of iron-chromium steels to nitric acid. W. Guertler and W. Ackermann's results with nitric acid (sp. gr. 1·005 and 1·12), and with sulphuric acid (sp. gr. 1·005) are summarized in Fig. 265. P. Kötzschke found that nickel decreases the corrodibility by conc. alkali-lye 88 per cent. According to C. Duisberg, iron with 5 per cent. nickel is very resistant towards soln. of sodium hydroxide; and, according to W. Fröhlich, high nickel-steel is less affected by contact with hydrogen and nitrogen than is the case with ordinary steel. The subject was studied by J. L. Everhast, and H. E. Searle and R. Worthington. J. S. Vanick investigated

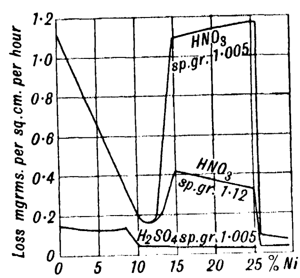


FIG. 265.—Action of Acids on Nickel-Iron Alloys.

attack by hot gaseous ammonia. D. J. McAdam discussed the corrosion of nickel-steels while under the influence of cyclic stress; and T. S. Fuller, the action of steam on the endurance tests. R. Vogel and H. Bauer studied the iron-nickel phosphorus system; and M. V. Ruisakoff and I. N. Buschmakin, the action of phosphorus and of phosphoric acid. H. M. Duncan studied the action of molten brass on nickel-steel; and H. Grubitsch, the action of zinc.

Le Société Anonyme le Ferronickel [23] prepared a **copper-nickel-iron alloy** with 55 : 2 : 25; R. Walter, H. F. Porter, W. P. Digby, J. J. Olsen, R. W. Leonard, and G. M. Colvocoresses described the manufacture of copper-nickel-steel—called *nicu*—from the Sudbury nickel-copper ores; T. Moore also prepared an alloy; and L. E. Stout and C. L. Faust, and H. Paweck and co-workers, the electrodeposition of the alloys. R. Vogel studied the ternary system, and the results are summarized in Fig. 266. The limits of saturation of the ternary solid soln. is a curve which starts from 96·5 per cent. of iron and 3·5 per cent. of copper, cutting through the nickel diagonal at 40 per cent. of nickel, and ends at 2·75 per cent. of iron and 97·25 per cent. of copper. All alloys falling outside this curve are homogeneous if sufficiently annealed. The alloy with Fe, 72; Ni, 24; and Cu, 4, has a structure resembling martensite when it is etched with nitric acid. The unsaturated soln. of medium composition are tough, and the crystals can suffer much deformation without rupture. All the alloys are magnetic at ordinary temp. The subject was studied by M. Tasaki, F. Roll, W. Köster and W. Dannöhl, and J. Asato. A. le Chatelier observed that with an alloy of Cu, 63; Ni, 34; Fe, 3, the tensile strength and elongation were:

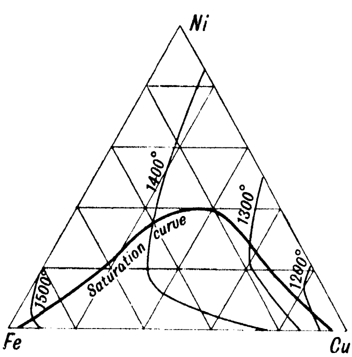


FIG. 266.—The Ternary System: Ni–Fe–Cu.

	15°	100°	150°	200°	250°	300°	350°	400°	460°
Tensile strength .	42·4	42·2	41·5	40·6	39·2	37	28	18·2	18 grms.
Elongation . .	40	31	31	34	30	23	20	15	3 per cent.

Observations were made by G. H. Clamer, J. A. Mathews, C. F. Burgess and J. Aston, G. A. Roush, G. M. Colvocoresses, J. C. Kolbe, O. Dahl and co-workers, and W. C. Chase. P. Chévenard studied the effect of copper on the dilation of ferronickels. He also observed that two mutually soluble phases are formed. H. le Chatelier also found that the Cu, 70; Ni, 18; Fe, 11 alloy had a transformation temp. of 690°, and that the electrical resistance from that point rises more rapidly than before. G. A. Roush measured the hardness of the alloys. P. R. Kosting found that the addition of copper to invar—36 Ni, 64 Fe—gave the following values for the thermal expansion coeff. from room temp. to 150° in cm. per cm. per degree:

Copper . .	0	7	15	38	48	60 per cent.
$\alpha \times 10^{-6}$ . .	1·9	3·2	5·4	9·9	11·3	22·0

The results for the electrical resistance in microhms per cm. cube at 20° are summarized in Fig. 267; and those for the temp. coeff. of the resistance in ohms per ohm per degree $\times 10^4$, in Fig. 268. W. C. Ellis and co-workers found the sp. ht. of the Ni-Cu-Fe, 70 : 28 : 2 alloy to be 0·132; the sp. gr., 8·94; the thermal conductivity, 0·0832; and the electrical conductivity, $2{\cdot}306 \times 10^4$ mho. Additions of up to 15 per cent. of iron decrease the sp. resistance and the thermoelectric force against copper, but increase the temp. coeff. of the resistance. The addition of up to 22 per cent. of copper to invar decreases the resistance, but increases the temp. coeff. of the resistance, the thermoelectric force, the coeff. of expansion, and

the temp. at which the expansion suddenly ceases. Observations were made by R. Ruer and C. Fick, S. W. Booth, N. B. Pilling, T. Chu, F. Ribbeck, L. R. Ingersoll, K. Feussner and S. Lindeck, and W. B. Earnshaw. P. R. Kosting's values

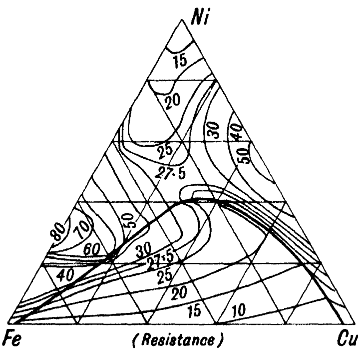


Fig. 267.—The Specific Resistance of the Copper-Nickel-Iron Alloys.

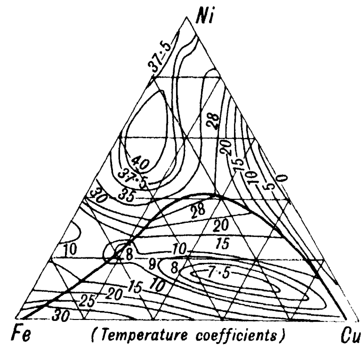


Fig. 268.—The Temperature Coefficient of the Resistance of the Copper-Nickel-Iron Alloys.

for the thermoelectric force in microvolts per degree are shown in Fig. 269. Small additions of iron to non-magnetic copper-nickel alloys make them magnetic. E. H. and A. H. Cowles and C. F. Mabery found that the addition of aluminium makes the alloy malleable. These quaternary **Cu–Ni–Fe–Al alloys** were discussed by W. Ruebel, and A. Jacobsen. The alloy with 2 gram-atoms each of copper and iron and 1 gram-atom each of nickel and aluminium resists attack by moist air, water, sea-water, and many acids. The quaternary **Cu–Ni–Fe–Mn alloys** were examined by E. L. Nichols who found the temp. coeff. of the electrical resistance of an alloy with copper, 78·28 ; ferromanganese, 14·07 ; and nickel, 7·65, is smaller than that of copper-iron-manganese, being $-0{\cdot}0_{4}11$ for the hard alloy, and $0{\cdot}0_{4}7$ for the annealed alloy; whilst for the alloy with copper, 52·51 ; ferromanganese, 31·27 ; and nickel, 12·22, the temp. coeff. of the hard alloy was $-0{\cdot}0_{4}39$ and of the annealed alloy $-0{\cdot}0_{4}32$. A. Pepe studied the thermoelectric properties. D. F. McFarland and O. E. Harder, V. Fischer, and E. Weston made observations on the subject. M. Kersten, and A. Kussmann and B. Scharnoff studied the magnetic properties. J. A. Jones observed that the introduction of copper to nickel-steel did not increase the resistance to corrosion, but the copper was not detrimental to the mechanical properties. Observations on the effect of sea-water were made by J. A. N. Friend and W. West.

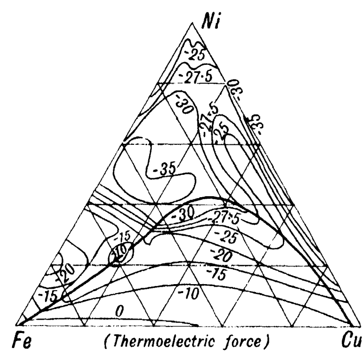


Fig. 269.—The Thermoelectric Force of the Copper-Nickel-Iron Alloys.

M. E. Barker studied the **iron-nickel-silver alloys** ; and B. Jones, J. H. S. Dickenson and W. H. Hatfield, and W. Kroll, the **iron-nickel-beryllium alloys.** O. L. Erdmann examined the quaternary **Cu–Ni–Fe–Zn alloys,** and found that iron does not readily alloy with nickel-silver. K. Feussner and S. Lindeck found that the sp. resistance of *rheotan*—Cu, 53·28 ; Ni, 25·31 ; Zn, 16·89 ; Fe, 4·46 ; Mn, 0·37—is 52·5 microhms per cm. cube, and the temp. coeff. is 0·00041. G. Niccolai observed that the electrical resistance, *R* c.g.s. units, is :

	400°	300°	200°	100°	0°	−100°	−189°
R . .	48,200	48,090	47,195	45,910	44,645	43,373	42,198

H. Brion studied the Barkhausen effect. The quinary Cu-Ni-Zn-Fe-Al alloys examined by A. Jacobsen, and W. Ruebel have the hardness, tensile strength, and working properties of bronze, and they resist attack by chemical reagents very well. The quinary Cu-Ni-Zn-Fe-Mn alloys were examined by A. Jacobsen, and E. Priwoznik. G. Toucas found that the quinary Cu-Ni-Fe-Pb-Sn alloy (5 : 4 : 1 : 1 : 1) is silver-white, hard, and malleable. The trade-name *aphtit* refers to an alloy Fe, 66 ; Ni, 23 ; Cu, 5 ; W, 4.

N. Tschischewsky and S. Mikhailowsky [24] studied some **iron-nickel-boron alloys.** L. Guillet prepared **nickel-aluminium steels** with about 0·18 and 0·40 per cent. of carbon, and found that when forged in the usual way, the structure is pearlitic, not martensitic. Aluminium thus retards the formation of martensite by raising the transformation temp. which are lowered by nickel alone. The pearlite closes up on itself, becoming granular, and more and more compact like sorbite or troostite. The steels are martensitic after quenching from 850° when the proportion of aluminium does not exceed 1 per cent. ; with more aluminium, the conversion to martensite is partial ; and with over 5 per cent. of aluminium, no martensite is formed. The higher the proportion of aluminium, the less is the influence of annealing on the pearlite. The mechanical properties show that the tensile strength and elastic limit are high, and the elongations are low, particularly when the pearlite becomes granular. The resistance to shock is low. The presence of aluminium hinders cementation to a marked degree. In no instance was the martensite structure developed in case-hardening, but the steels contained a confused mass of pearlite mixed with more or less cementite. The alloys do not promise to be of industrial value. P. Chévenard observed the formation of two mutually soluble phases. E. Vaders studied the age hardening of the alloys ; W. Köster, V. S. Messkin, B. E. Somin, and J. H. Rabbit and T. Fujiwara, the magnetization ; E. Vaders, T. H. Chilton and W. R. Huey, F. Krupp, T. Sato, and V. Fuss, the properties of some of these alloys ; J. S. Vanick, the action of hot, gaseous ammonia ; G. R. Brophy described the manufacture and properties of *calite*, the trade-name for an alloy of iron, nickel, and aluminium ; and V. Perchké, and E. Vaders studied the **iron-nickel-aluminium-copper alloys** ; G. Guzzoni, the **nickel-aluminium-magnesium alloys** ; and I. Tscherkesoff, the **iron-nickel-tin-copper alloys.**

L. Guillet prepared **nickel-silicon steels** with about 0·2, 0·4, and 0·9 per cent. of carbon. Structurally, these steels can be ranged in seven classes : (i) pearlitic steels ; (ii) steels with pearlite and graphite ; (iii) steels with all the carbon as graphite ; (iv) martensitic steels ; (v) steels with martensite, graphite, and possibly also ferrite ; (vi) steels containing polyhedra of γ-iron ; and (vii) steels with polyhedra of γ-iron, graphite, and possibly also ferrite and martensite. The steels with γ-iron show also white specks thought to be a silicide. The silicon raises the transformation points of nickel steels, and thus alters the percentage of nickel corresponding to which transformation, from one structure to another, occurs. Silicon thus facilitates the transformation of γ-iron-nickel-steel into a steel containing martensite, yet at the same time, it retards the formation of martensite. Nickel impedes the precipitation of carbon as graphite, particularly in pearlitic and martensitic steels. The presence of graphite in a nickel-silicon steel depends on the percentage of silicon and also of carbon. For constant proportion of nickel, less silicon is needed to produce graphite the higher is the proportion of carbon present. Silicon in nickel-steel allows of a greater effect being obtained on quenching, but this is at the expense of the resistance to shock particularly at right angles to the plane of rolling. Prolonged annealing at 900° does not alter the condition of the carbon in the nickel-silicon steels used for the experiments. This is the opposite to what obtains with silicon steels. The mechanical tests show that the pearlitic steels have a tensile strength and elastic limit higher than is the case with steels containing nickel only, but the elongation and resistance to shock are lower. The martensitic steels have a great tensile strength, but are very

brittle, particularly in a direction at right angles to the plane of rolling. Steels with γ-iron are if anything improved by silicon which raises their tensile strength. Quenching from 800° in water at 20° has a marked effect on the pearlitic steels, for it raises very much the tensile strength and elastic limit, but reduces the elongation so that the steels become rather brittle. Their steels offer a fair resistance to shock even when the elongation is zero; and the resistance to shock in a direction perpendicular to the plane of rolling is also zero. Quenching has the same effect on martensitic steels, and on those containing γ-iron, as it has on steels with nickel only. Once a martensitic or γ-iron nickel-silicon steel has graphitized, it can no longer be forged; this is not the case with the pearlitic steels. The addition of silicon to nickel-steels is not to be recommended. R. Harrison, and A. B. Everest and co-workers discussed their mechanical properties; S. Guggenheim, and H. Kühlewein, the magnetic properties; and W. B. Earnshaw, their resistance to chemical corrosive agents.

M. A. Hunter and J. W. Bacon studied the magnetic properties of the **nickel-iron-titanium alloys.** E. W. von Siemens and J. G. Halske prepared **nickel-iron-tantalum alloys** by adding a nickel-tantalum alloy to molten iron or steel. The tantalum oxidized less readily when it is added to the alloy with nickel than when it is added alone to the iron or steel, and the amount may be more accurately regulated. An alloy, with Ta, 10; Ni, 10; and Fe, or steel, 80, is exceptionally tough, elastic, and hard. It is suitable for the manufacture of implements, and tools.

L. Guillet prepared **nickel-iron-vanadium alloys** with the carbon ranging from 0·140 to 1·251 per cent. They can be ranged in six classes according to their microstructure: (i) pearlitic steels; (ii) steels with pearlite and carbide; (iii) martensitic steels; (iv) steels with martensite and carbide; (v) steels with polyhedra of γ-iron; and (vi) steels with polyhedra of γ-iron and carbide. If the proportion of vanadium is high enough, all the carbon will be precipitated as carbide. It was thought that if enough vanadium be added to a nickel-steel containing γ-iron, the percentage of carbon would be reduced by the formation of vanadium carbide, and if the percentage of nickel were suitable, the steel would become martensitic. This was not the case. A state of equilibrium is attained which is not destroyed by the vanadium. In normal steels with rather less than 0·19 per cent. of carbon, and 6 per cent. of nickel, the addition of up to 0·68 per cent. of vanadium makes the steels rather more inclined to become martensitic, which is more pronounced the higher is the proportion of vanadium. Steels with about 0·4 per cent. of carbon, 3 per cent. of nickel, and up to 0·68 per cent. of vanadium are pearlitic, and where the vanadium is highest, there is a feeble tendency to form martensite. All samples quenched from 850° were martensitic. Annealing did not affect the steels beyond coarsening the grain-size of the pearlite and martensite. The mechanical tests show that vanadium distinctly raises the tensile strength and elastic limit of pearlitic steels more rapidly than any element other than carbon; and at the same time, it slightly lowers the elongation and reduction of area, although much less so, other things being equal, than other elements. The maximum effect is obtained with 0·7 to 1·0 per cent. of vanadium, and it diminishes as the carbon passes into carbide. Vanadium acts similarly on martensitic steels, but the effect is less marked; and with γ-iron steels, it slightly raises the elastic limit, but at the same time distinctly lowers the elongation and induces brittleness. The results with quenched steels show that the mechanical properties are greatly influenced by vanadium, and that the best results are obtained when the proportion of carbon is low, since otherwise the high tensile strength and elastic limit are counterbalanced by a decreased elongation and resistance to shock. The mechanical properties of the annealed steel are but little affected by vanadium. Consequently the best results of all are obtained with the pearlitic steels; and with quenched pearlitic steels containing a small proportion of vanadium, the tensile strength is markedly increased, while the elongations are

fair, and the resistance to shock is good. In case-hardening, small zones of martensite and of γ-iron are formed, but the main structure is pearlite or troostite with needles of cementite. L. Guillet considers that these steels should be industrially important; and they were studied by J. Challansonnet, H. Kühlewein, and J. Strauss. H. Kühlewein studied the ternary system. R. W. Moffatt found that the resistance to impact at a low temp. is high. H. J. French made some tensile strength and creep tests. J. Challansonnet found that cast iron with and without nickel shows eutectic cementite and dendrites of pearlite; but cast iron, containing vanadium, shows cementite only. The addition of 1 to 2 per cent. of nickel had no influence on the Curie point of cementite, but the addition of 0·25 and 0·50 per cent. of vanadium lowered the Curie point by 160° and 130° respectively. Nickel does not modify this effect of vanadium and cementite, but nickel lowers the Ac- and the Ar-points. Vanadium alone has no effect on these points, but if they have been lowered by nickel, it raises them. Nickel lowers the temp. of graphitization, but vanadium prevents the graphitization of iron with 3·75 per cent. carbon at temp. up to 1800°; it thus increases the temp. of graphitization in opposition to the graphitizing effect of nickel. One part of vanadium annuls the effect of four parts of nickel. Observations were also made by J. Challansonnet, and H. Lange and F. Wever.

W. Ritter prepared the **nickel-chromium-iron alloys** in hydrogen gas. L. Guillet investigated the nickel-chromium steels containing 0·20 and 0·80 per cent. of carbon. The microstructures which he observed were (i) pearlite; (ii) pearlite with carbide; (iii) martensite; (iv) martensite with carbide; (v) polyhedra of γ-iron; and (vi) polyhedra of γ-iron with carbide. Pearlite was never observed in the hypoeutectoidal steels. The transformation from pearlite to martensite depends on the sum of the elements added to iron, namely, carbon, nickel, and chromium. The addition of chromium to a nickel martensitic steel produces a carbide in quantities depending on the proportion of carbon in the steel; and with larger proportions, the chromium adds its effect to that of nickel producing polyhedra of γ-iron; likewise also with the steels containing γ-iron. The carbide separates when a certain percentage of chromium is reached; the actual amount depends on the percentage of carbon in the metal. The percentage of carbon in a nickel-chromium steel is always distinctly lower than that of an analogous steel free from nickel. Nickel-chromium steels with a high proportion of carbon, and enclosing carbide, do not show after etching with picric acid the black background, resembling troostite, observed in the case of chromium steels. Nor does this constituent ever occur with the martensitic nickel-chromium steels. When the pearlitic steels are quenched from 860°, the pearlite is transformed into martensite which is coarser grained, the larger the sum of the nickel, chromium, and carbon. The quenching of martensitic steels which do not undergo transformation has a tendency to form polyhedra of γ-iron, or of small whitish areas. Steels with martensite and carbide are not transformed on quenching from 850°, but the carbide disappears with the production of γ-iron once the quenching temp. reaches 1200°. Steels with polyhedra of γ-iron are not altered by quenching, but if carbide is present, and the quenching temp. attains 1200°, a transformation occurs. Annealing, sufficiently prolonged, and at a high enough temp., disseminates the grains of carbide more uniformly, and it also intensifies the polyhedral structure, and causes the carbide grains to arrange themselves more regularly and uniformly round the edges of the polyhedra. According to R. H. Russell, steels with up to 8 per cent. of chromium and nickel are pearlitic; with between 8 and 20 per cent., martensitic; and with up to 25 per cent., austenitic. F. Leitner discussed the formation of primary crystallites in the solidification of the molten metal; O. Smalley, the influence of the dendritic structure on the physical properties; P. Bardenhauer, flakes in the steels; C. F. Brush, the spontaneous development of heat in a recently-hardened alloy; and A. N. Masloff, the transformation points of nickel-chromium steel. The subject was studied by J. H. Andrew and

H. A. Dickie, J. H. Andrew and H. Hyman, G. d'Ardigny, A. L. Baboshin, E. C. Bain and W. E. Griffiths, K. Bischoff, H. M. Boylston, E. Bremer, H. C. H. Carpenter, P. Chévenard, F. B. Coyle, L. le Coz, A. P. Davis, J. S. Ewing, L. Guillet and A. M. Portevin, L. Guillet and co-workers, R. A. Hadfield, E. Houdremont, E. Houdremont and H. Kallen, J. H. Hruska, N. V. Hybinette, V. Koseleff and F. Poboril, E. Kothny, E. C. Kreutzberg, V. N. Krivobok, F. Krupp, R. M. Major, J. A. Mathews, P. D. Merica and co-workers, G. Nesselshtrauss, A. L. Norbury and E. Morgan, B. Palmgren, H. D. Phillips, N. B. Pilling, J. Pomey and P. Voulet (Fig. 270), W. Raedeker, W. Rohn, F. Sauerwald and co-workers, W. S. Smith and co-workers, R. L. Spitzley and A. M. Thompson, B. Strauss and co-workers, M. Tasaki, J. S. Vanick, W. Venator, M. Wählert, R. Wijkander, and W. H. Wills and J. K. Findley. J. Pomey and P. Voulet's ternary diagram is shown in Fig. 270, where the region (1) represents a solid soln. of α-ferrite, stable at all temp. and isomorphous with α-iron and chromium; (2) α-phase of ferrite or martensite transformable entirely into austenite at temp. exceeding A_3 (pearlitic and martensitic steels); (3) α-phase of ferrite or martensite transformable entirely into austenite at temp. above A_3, and, at least partially, into δ-iron by heating above A_4 (pearlitic and martensitic steels); (4) α-phase partially transformable into austenite at a high temp.; (5) solid soln. of γ-iron stable at all temp. isomorphous with nickel, and forming the reversible chromium-iron-nickel alloys; (6) γ-phase metastable at ordinary temp., transformable into the α-phase by cold work or by cooling to a low temp., and forming irreversible chromium-iron-nickel alloys; (7) metastable γ-phase like the preceding, but it can be transformed into the δ-phase at a high temp.; (8) a mixture of metastable α- and γ-phases, the proportion varying with the temp. of tempering; and (9) a mixture of the two phases (1) and

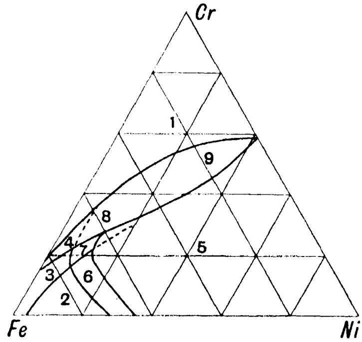


FIG. 270.—The Equilibrium Diagram of the System: Fe–Cr–Ni.

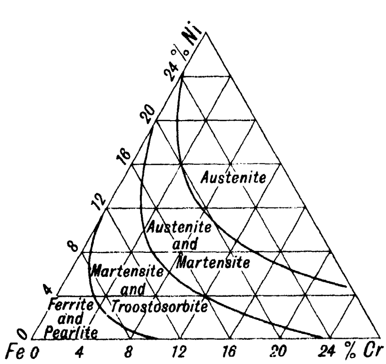


FIG. 271.—Constituents of Chromium-Nickel Steels.

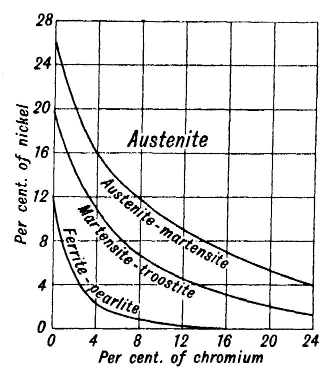


FIG. 272.—Constituents of the Quaternary System: Fe–Cr–Ni–C Alloys.

(5), isomorphous with chromium and nickel. B. Strauss and E. Maurer represented the structure of chromium-nickel steels containing a small proportion of carbon by a diagram which corresponds with that of E. H. Schulz and W. Jenge, Figs. 271 and 272. J. H. Andrew and D. Binnie obtained similar results with nickel-chromium steels as they did with nickel-steels (*q.v.*).

A. Dumas observed that chromium acts on the irreversible nickel-steels—with up to 25 per cent. of nickel—by lowering the transformation temp., but with the

reversible nickel-steels it raises this temp. L. Guillet found that the action of chromium is not proportional to the amount added, and with steels containing 3 to 5 per cent. of nickel, the influence is very slight, but it is greater when the proportion of nickel is raised. The nickel-chromium steels form three classes: (i) those in which the transformation points on heating and cooling are nearly the same—*e.g.*, the pearlitic steels; (ii) those in which this difference increases up to 500° proportionally with the chromium content—*e.g.*, the martensitic steels; and (iii) those which still show a difference but the influence is very slight—*e.g.*, steels containing carbide, and in which the chromium is not all in soln. The martensite structure commences when the transformation point on cooling is about 350°. The steels in Fig. 272 had 0·3 to 0·6 per cent. of carbon. F. Wever and W. Jellinghaus represented the phases in the ternary system at room temp., by Fig. 273. The effect of nickel and chromium on the transition points has been discussed by W. T. Griffiths, B. Egeberg, V. N. Krivobok and co-workers, and others—*vide supra*, the constituents of the iron-carbon alloys; the effect of carbon, by T. Murakami and M. Mikami; the effect of deoxidizing agents, by W. Oertel and L. A. Richter; and the effects of beryllium, boron, and titanium, by H. Bennek, and P. Schafmeister.

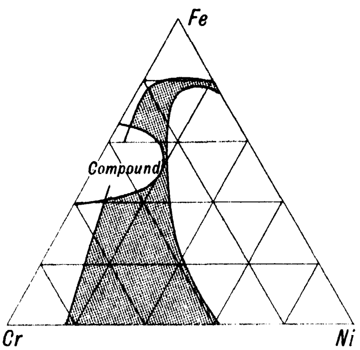


FIG. 273.—Phases in the Ternary System: Fe–Cr–Ni.

The so-called *enduro* is a trade-name for a chromium-nickel-iron alloy—*e.g.*, enduro has C, <0·12; Mn, <0·50; S, <0·03; P<0·03; Si, <0·50; Cr, 17 to 19; and Ni, 8 to 9 per cent. W. C. Ellis and co-workers gave 8·40 for the sp. gr. of the Fe : Ni : Cr (26 : 62 : 12) alloy. The mechanical properties were studied by L. Guillet, who found that in pearlitic steels, with up to 5 per cent. nickel, the influence of chromium reinforces that of nickel. Comparing the results with nickel-steels possessing the same structure, the chromium raises the tensile strength, elastic limit, and hardness without appreciably lowering the elongation and resistance to shock. The chromium does not affect the martensitic steels (12 per cent. nickel) so much. With steels containing γ-iron, chromium raises the tensile strength and elastic limit, slightly lowers the elongation, but still leaves the reduction of area, and resistance to shock high. Steels containing carbide, whether they are martensite or contain γ-iron, become brittle even though their elongation and reduction of area is fairly high. When quenched from 860°, the tensile strength, elastic limit, and hardness of the martensitic steels are increased by chromium, whereas the elongation, and reduction of area fall slightly. The increase in the tensile strength of the martensitic steels by quenching is attributed to the quenching process making the solid soln. homogeneous. Quenching if anything, softens martensitic steels containing carbide, but without changing their structure very much. The hardness is augmented. Steels containing polyhedra of γ-iron are slightly softened by quenching. Annealing for 4 hrs. at 900° softens all the chromium-nickel steels, but makes itself felt principally with steels containing γ-iron; with the other steels, annealing diminishes the tensile strength, but affects the elastic limit only slightly; the elongation, and reduction of area are slightly reduced. Cooling the steels to a low temp. does not produce effects resembling those which occur with nickel-steels of analogous composition, so that chromium hinders these transformations, and refrigeration has less influence on nickel-chromium steels than it has on the nickel-steels. Case-hardened steels containing martensite show in the case-hardened portion: grains of carbide, needles of troostosorbite and polyhedra of γ-iron. In the case-hardening of steels containing γ-iron, the polyhedra become large and are edged with carbide.

Towards the exterior of the martensite, this carbide spreads into the interior of the polyhedra, and becomes so abundant that it may mask the polyhedra. The polyhedra may exhibit twinning. The case-hardening of pearlitic steels furnishes a core of pearlite, then follows a transition zone of pearlite, and martensite ; then coarse-grained martensite ; then a zone of martensite and γ-iron ; and finally a zone of pearlite mingled with cementite. The subject was studied by E. Greulich and G. Bedeschi, K. Sasakawa, and B. Strauss and co-workers. The range of the Ac_1-arrest in the nickel-chromium steels was discussed by M. S. Aranovich and co-workers, R. H. Greaves, J. J. A. Jones, H. Lüpfert, H. Brearley, E. Maurer and co-workers, A. Merz, H. E. Potts, A. Reggiori, A. E. W. Smith, I. N. Golikoff, and M. Tamaki ; the grain-growth, by E. Greulich and G. Bedeschi ; and the decarbonization, by R. W. Dayton.

W. A. Dean studied the nickel-chromium system and found that the X-radiograms indicated the presence of three groups of crystals—body-centred, face-centred, and a mixture of the two. These zones are indicated in Fig. 274, where

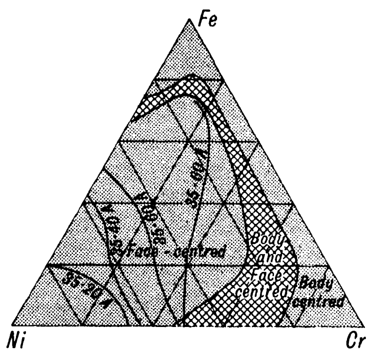


Fig. 274.—The Lattices and Lattice Parameters of the Nickel-Iron-Chromium Alloys.

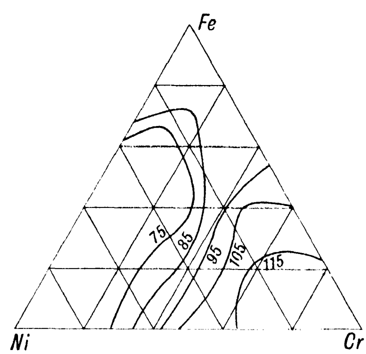


Fig. 275.—The Hardness of the Nickel-Iron-Chromium Alloys.

the face-centred lattice of nickel dominates the system. The dimensions of the lattice parameter in A-units are also indicated in the diagram. H. Perlitz, M. Vialle and A. van den Bosch, J. R. Vilella, and J. Splichal and F. Cabicar studied the X-radiograms ; and H. Esser and co-workers, the effect of flecks. The values for the Rockwell hardness of the alloys are indicated in Fig. 275. T. Murakami and M. Mikami studied the effect of carbon on the hardness. Observations on the hardness and other mechanical properties have been made by the following :

A. Abraham, L. Aisenstein and E. Decherf, L. Aitchison, J. H. Andrew and co-workers, M. S. Aranovich and co-workers, H. Brearley, M. Brès, C. B. Callomon, H. Chase, M. Chaussain, P. Chévenard and co-workers, E. W. Colbeck and co-workers, J. Cournot and co-workers, C. A. Crawford and R. Worthington, H. C. Cross, W. A. Dean, J. H. S. Dickenson, H. A. Dickie, T. G. Digges, J. W. Donaldson, S. F. Dorey, H. Edert, N. Elfström and P. E. Lagerhjelm, O. W. Ellis, P. Eyermann, H. J. French, H. J. French and co-workers, J. Galibourg, H. L. Geiger, P. Goerens, R. H. Greaves and co-workers, L. Grenet, E. Greulich and G. Bedeschi, W. T. Griffiths, M. A. Grossmann, L. Guillet and co-workers, H. Hanemann and R. Hinzmann, D. Hanson, W. H. Hatfield, H. K. Herschman, H. D. Hibbard, C. C. Hodgson, K. Honda, E. Houdremont and co-workers, J. V. Howard and S. L. Smith, F. A. Hütte, A. Hultgren, J. E. Hurst, N. N. Inshakoff, C. M. Johnson, J. J. A. Jones, L. Jordan, H. Jungbluth and A. Pomp, W. Kahlbaum and L. Jordan, H. Kalpers, O. von Keil and O. Jungwirth, G. H. Keulegan and M. R. Houseman, C. L. Kinney, G. Klein, E. Kothny, W. Kurose, E. F. Lake, F. C. Langenberg, F. C. Lea, F. Leitner, G. V. Luerssen and O. V. Greene, P. Ludwik, Y. Matsunaga, E. Maurer and W. Schmidt, C. McKnight, P. D. Merica, A. Michel and P. Benazet, R. Moldenke, R. R. Moore and E. V. Schaal, K. H. Müller and E. Piwowarsky, J. Negru, H. D. Newell, J. Ohly, B. Palmgren, O. K. Parmiter, J. W. Percy, C. W. Pfannenschmidt, E. W. Pierce, N. B. Pilling and co-workers, E. Piwowarsky, R. Plank, A. M. Portevin, V. Prever and C. A. Maresca, W. B. Price, H. B. Pulsifer and O. V. Greene,

W. Riede, F. Rogers, A. Rys, P. J. Saldau and V. N. Semenoff, K. Sasakawa, B. J. Sayles, P. Schafmeister and A. Gotta, H. Schallbroch, A. Schleicher, M. Schmidt and O. Jungwirth, W. Schneider and E. Houdremont, O. Schwarz, R. Sergeson, B. F. Shepherd, E. K. Smith and C. H. Aufderhaar, K. F. Starodubоff, B. Stoughton and W. E. Harvey, B. Strauss and E. Maurer, L. Thiéry, W. A. Tucker and S. E. Sinclair, T. H. Turner, H. Voss, H. Wentrup and W. Stenger, T. H. Wickenden and J. S. Vanick, W. H. Wills and J. K. Findley, T. J. Wood, A. G. Zima, and V. Zsak.

The sp. gr. and sp. vol. of the alloys were studied by J. H. Andrew and co-workers, H. A. Dickie, and R. H. Greaves and J. J. A. Jones. C. L. Clark and A. E. White studied the effect of temp. on the tensile strength ; A. Grunert, the effect of ageing ; F. Robin, the resistance to crushing ; H. H. Lester, the brittle range of the 8 to 18 per cent. chromium-nickel irons ; H. J. French and co-workers, and H. J. Tapsell and J. Remfry, the creep strength ; H. F. Moore and T. Ver, the slip-lines and strain-lines ; B. Strauss and co-workers, the carbide precipitation in cold-working ; E. Brüsewitz, the case-hardening of chromium-nickel steel ; and P. L. Irwin, H. J. Gough and D. G. Sopwith, and N. P. Inglis and G. F. Lake, the corrosion-fatigue in river water, etc. The brittleness of alloys with less than 0·1 per cent. of carbon was studied by H. H. Lester. L. Aitchison and L. W. Johnson compared the strength of bars taken longitudinally and transversely to the direction of rolling or forging. For T. Kawai's observations on the impact test of these steels, *vide* the impact test of iron. J. Cournot and K. Sasagawa studied the viscosity of the alloys ; J. H. S. Dickenson, H. C. Loudenbeck, and H. F. Moore and A. G. Gehrig, the effect of heat treatment on the properties of the alloys. For the temper-brittleness of these steels, *vide* tempering. F. Rogers observed that 0·38 per cent. of vanadium made no difference to the temper-brittleness. For J. H. Andrew and co-workers' observations on the effect of the temp. on the physical properties, *vide* the physical properties of iron, **13.** 66, 18 ; A. S. Predvoditeleef studied the heat conductivity ; H. Miyabe, the thermal emission of positive ions ; and C. L. Clark and A. E. White, the proportional limits of different carbon alloy steels, and the results are summarized in Fig. 276.

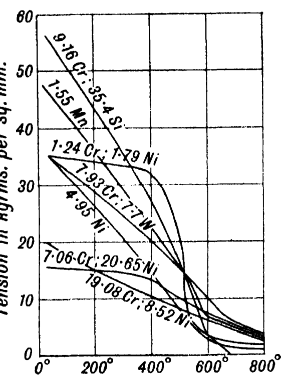


FIG. 276.—The Proportional Limits of Carbon Alloy Steels.

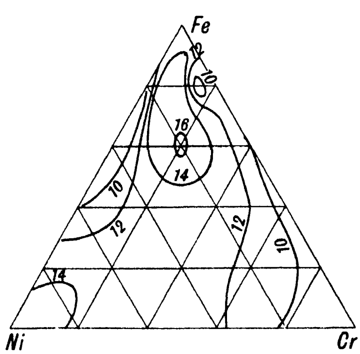


FIG. 277.—The Coefficient of Thermal Expansion of the Nickel-Iron-Chromium Alloys.

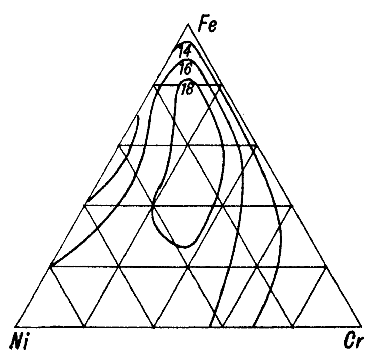


FIG. 278.—Thermal Expansion of the Nickel-Iron-Chromium Alloys at 1000°.

L. Aitchison and G. R. Woodvine, A. Michel and P. Benazet, and E. Houdremont and E. Bürklin discussed the changes in vol. during the heat treatment of the alloys ; and P. Chévenard, the dilatometric anomalies at 550°. J. A. Mathews studied the thermal expansion, and W. A. Dean gave the results indicated in Fig. 277 for the coeff. of thermal expansion, $\delta \times 10^6$ per degree between 20° and

100°, and in Fig. 278 for the expansion at 1000° expressed as $(\delta l/l)\times 10^3$. H. J. French, V. N. Krivobok and S. M. Gensamer, P. Hidnert, J. B. Austin and R. H. H. Pierce, and W. H. Souder and P. Hidnert also measured the thermal expansion of these alloys. T. J. Wood studied the growth of nickel-chromium-iron alloys. W. C. Ellis and co-workers gave for the Fe : Ni : Cr (26 : 62 : 12) alloy, the sp. ht. 0·107; and the thermal conductivity, 0·0325. S. M. Shelton, and M. S. van Dusen and S. M. Shelton studied the subject. F. Wever and W. Jellinghaus found the isotherms of the liquidus curves of the alloys shown in Fig. 279; and the thickened line in the same diagram represents the m.p. curve of the alloys. The shaded portion represents the region of the α- and γ-phases.

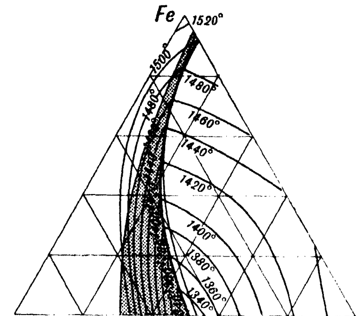


FIG. 279.—Isotherms of the Liquidus Surfaces of the Ternary Alloys.

W. C. Ellis and co-workers found the electrical conductivity to be $k\times 10^{-5}=0{\cdot}0911$ mho. The electric, thermoelectric, and magnetic properties of the alloys were studied by A. Abt, H. Brearley, C. W. Burrows and F. P. Fahy, E. D. Campbell and H. W. Mohr, P. Chévenard, E. Colver-Glauert and S. Hilpert, H. A. Dickie, R. L. Dowdell, E. Dumont, N. J. Gebert, R. H. Greaves and J. J. A. Jones, L. Grenet, W. C. Hirsch, K. Honda and R. Yamada, Z. Jeffries and R. S. Archer, J. F. Kayser, A. M. Korolkoff, E. Marcotte, R. Müller and co-workers, E. F. Northrup, W. Rohn, M. Sauvageot and L. Lauprète, C. J. Smithells, W. H. Stannard, T. H. Turner, F. Wever and H. Lange, and T. D. Yensen. W. A. Dean's results for the electrical resistance of the alloys in microhms per cm. cube, at 20°, are summarized in Fig. 280, and for the temp. coeff. of the resistance, $a\times 10^4$, per degree between 20° and 100° in Fig. 281. A. Schulze, M. A. Hunter

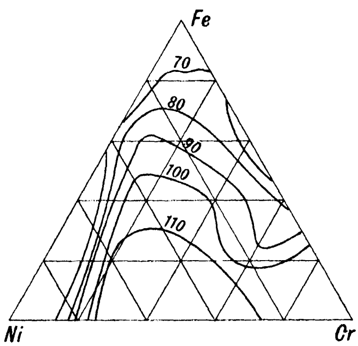


FIG. 280.—The Electrical Resistance of the Nickel-Iron-Chromium Alloys.

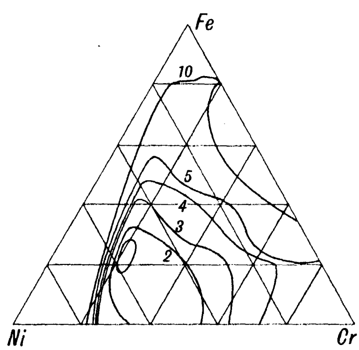


FIG. 281.—The Temperature Coefficient of the Resistance of the Nickel-Iron-Chromium Alloys.

and A. Jones, L. O. Hart, and W. A. Gatward made observations on the electrical resistance. M. A. Hunter and A. Jones found the resistance, R, of alloys with Ni : Fe : Cr=53·58 : 13·7 : 31·35 and 27·62 : 48·45 : 21·10, to be respectively :

	20°	300°	400°	500°	600°	700°	800°	900°	1000°
R .	1·00	1·048	1·061	1·075	1·076	1·079	1·084	1·090	1·098
	1·00	1·120	1·154	1·182	1·208	1·227	1·247	1·266	1·284

P. W. Bridgman found for the so-called *comet alloy*—Cr, 1·75; Ni, 31 to 32; C, 0·20 to 0·25; Si, 0·20 to 0·25; Mn, 1·8 to 2·0; traces of P and S; and the remaining percentage, iron—the resistance unity at 0° is 1·04644 at 50°, and 1·09061 at 100°. The press. coeff. at 0 and 12,000 kgrms. per sq. mm. are respectively $-0{\cdot}0_{5}263$ and $-0{\cdot}0_{5}222$ at 0°; $-0{\cdot}0_{5}224$ and $-0{\cdot}0_{5}206$ at 50°; and

$-0{\cdot}0_5203$ and $-0{\cdot}0_5194$ at 100°. For the alloy with Fe, 68; Ni, 30; Cr, 2, he found at 94·2°, the average press. coeff. of the electrical resistance from 0 to 12,000 kgrms. per sq. cm., $-0{\cdot}0_51790$; and the temp. coeff. of the resistance between 0° and 94° is 0·006684. L. O. Hart, and P. Nicolau studied the thermoelectric force. The measurements of M. A. Hunter and A. Jones on the thermoelectric force of the alloys against copper are summarized in Fig. 49. E. Liebreich found the potential of nickel-chromium steels in N-$FeSO_4$ to be —0·31 to +0·48 volt. A carbon content of 0·4 per cent. almost eliminates the passivity of 13 per cent. chromium steels, and the presence of oxygen in the electrolyte reduces the percentage of chromium necessary for passivation; in hydrogen, passivation does not occur with higher proportions of chromium. The chromium-nickel steels resemble passive chromium rather than iron or active chromium. B. Strauss observed that the potential of steels with 20 per cent. of chromium and 7 per cent. of nickel in N-$FeSO_4$ against a 0·1N-calomel electrode, 0·2 volt was obtained when up to 1 per cent. of carbon was present, and —0·6 volt with over 2 per cent. of carbon. O. von Auwers, P. Chévenard, J. M. Ide, P. Kapitza, T. Matsushita and K. Nagasawa, V. S. Meskin and E. S. Tovpenetz, C. Sadron, J. Safraneck, J. Seigle, and F. Wever and W. Jellinghaus studied the magnetic properties; and V. S. Messkin and co-workers, the magnet steels. W. A. Dean's results for the magnetostriction are summarized in Fig. 282. The phenomenon is confined to the

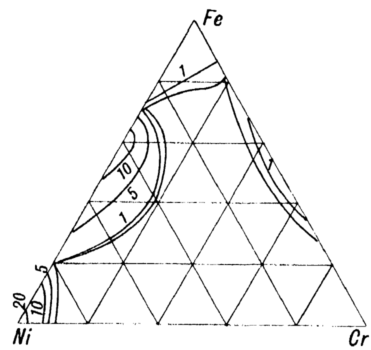


FIG. 282.—The Magnetostriction of the Nickel-Iron-Chromium Alloys.

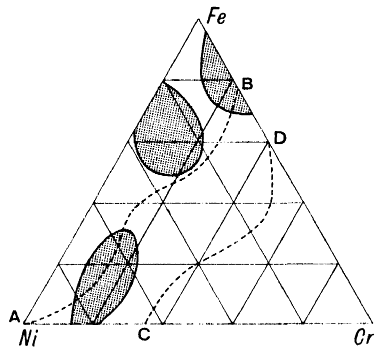


FIG. 283.—The Heat Resistance of the Nickel-Iron-Chromium Alloys.

iron-chromium and iron-nickel alloys and to the adjacent ternary alloys with not over 10 per cent. of the third component.

Some observations on the action of chemical agents on the nickel-chromium steels, and the passivity of these alloys, have been discussed in connection with stainless steels, and in connection with corrosion. L. Jacqué studied the action of hydrogen; and M. S. Kice, corrosive gases. W. A. Dean said that alloys with 20 to 40 per cent. of chromium and up to 55 per cent. of nickel resist oxidation at 1000° as well as more expensive alloys. The alloys to the right of the dotted line AB, Fig. 283, resist oxidation at 1000° comparably with the standard heat-resisting alloys on the market; and the dotted line CD represents those alloys which could be cold-rolled so that the area $ABCD$ represents heat-resisting alloys which can be rolled and forged. The stippled areas in the diagram represent areas which include thirty commercial heat-resisting alloys. L. B. Pfeil observed that a three-layer scale is formed when nickel-chromium steel is heated at 1000° for several hours in air. The two outer layers contained less than one-tenth of the nickel and chromium present in the innermost layer, whilst the latter contained, relative to the iron, three times as much nickel and chromium as the original steel. W. Hessenbruch and E. Horst studied the intercrystalline corrosion. J. E. Stead also noted the accumulation of nickel in the outer layers at 800° to 1000°. Y. Utida and M. Saito studied the tendency to oxidation when

the alloys are heated for an hour at 1100° in air. H. Ipavic studied the resistance towards hydrogen sulphide. Y. Utida and M. Saito made observations with 10 per cent. soln. of nitric, hydrochloric, and sulphuric acid, at room temp., and expressed the results as loss in weight in grams per sq. cm. in 24 hrs. The results are collected in Table XX. These alloys contained approximately 0·1 per cent.

Table XX.—The Action of Acids and Air on Nickel-Chromium Steels. (Approximately 0·1 Per Cent. of Carbon.)

Approximate percentage nickel	Chromium (per cent.)	Grams loss per sq. cm. per 24 hrs.			Grams gain per sq. cm. per hour at 1100°
		HNO_3	HCl	H_2SO_4	
4·0	8·9	0·0045	0·0412	0·0470	0·0450
	11·20	0·0007	0·0460	0·0569	0·0451
	13·66	0·0000	0·0570	0·0440	0·0377
	15·36	0·0000	0·0682	0·0372	0·0118
	18·12	0·0000	0·0870	0·0368	0·0014
	22·80	0·0000	0·0430	0·0323	0·0007
	28·36	0·0000	0·0455	0·0054	0·0005
6·0	9·58	0·0055	0·0366	0·0435	0·0476
	11·68	0·0006	0·0233	0·0296	0·0407
	13·83	0·0000	0·0229	0·0206	0·0294
	17·78	0·0000	0·0258	0·0105	—
	20·55	0·0000	0·0342	0·0050	0·0010
	26·01	0·0000	0·0378	0·0042	0·0007
	32·04	0·0000	0·0648	0·0038	0·0009
10·0	10·18	0·0087	0·0182	0·0047	0·0275
	12·60	0·0004	0·0092	0·0034	0·0220
	15·83	0·0000	0·0060	0·0031	0·0098
	18·67	0·0000	0·0053	0·0031	0·0012
	21·95	0·0000	0·0058	0·0037	0·0010
	25·32	0·0000	0·0066	0·0048	0·0010
	27·98	0·0000	0·0076	0·0039	0·0008
13·5	9·04	0·0046	0·0035	0·0017	0·0334
	12·51	0·0002	0·0033	0·0019	0·0190
	14·95	0·0000	0·0037	0·0022	0·0026
	18·72	0·0000	0·0042	0·0023	0·0011
	21·80	0·0000	0·0048	0·0024	0·0006
	25·59	0·0000	0·0086	0·0023	0·0006
	28·10	0·0000	0·0094	0·0032	0·0006

Table XXI.—The Action of Reagents on Nickel-Chromium Steels.

Reagent	Hours exposure	C : Ni : Cr (per cent.)					
		0·14 : 0·42 : 14·51	0·47 : 5·34 : 18·54	0·97 : 19·71 : 11·63	0·48 : 39·13 : 8·28	0·20 : 54·38 : 12·44	0·15 : 62·2 : 12·40
Conductivity water	180	0·000	0·000	0·014	0·000	0·000	0·000
Sea-water	180	0·071	0·007	0·022	0·012	0·008	0·009
Sea-water	900	0·169	0·036	0·074	0·025	0·017	0·014
HNO_3 (1 : 1)	180	0·000	0·000	0·006	0·011	0·014	0·107
HNO_3 (conc.)	180	0·000	0·000	0·000	0·000	0·000	0·006
H_2SO_3	180	0·124	0·000	1·898	0·164	0·404	0·076
H_2SO_4 (1 : 10)	180	38·500	46·590	0·223	0·189	0·193	0·165
H_2SO_4 (conc.)	180	0·003	0·000	0·165	0·002	0·003	0·001
HCl (1 : 10)	180	8·525	1·592	0·284	0·141	0·217	0·210
HCl (conc.)	180	24·000	58·780	15·860	1·930	5·050	13·560
Acetic acid (80 per cent.)	180	0·002	1·000	1·898	0·696	0·628	0·573
Citric acid (1 : 2)	180	0·143	0·000	0·066	0·035	0·029	0·026
NH_4OH (conc.)	180	0·000	0·000	0·009	0·000	0·000	0·157
KOH (1 : 2)	180	0·000	0·000	0·000	0·000	0·000	0·000
Aqua regia	180	56·550	100·000	100·000	100·000	100·000	100·000

of carbon. The results can be recast to show chromium constant and nickel variable. J. A. N. Friend and co-workers found that the relative corrodibilities of steels with 3·4 per cent. nickel and 1·00 per cent. chromium, and with 3·5 per cent. nickel and 1·12 per cent. chromium, were with iron 100, with 6 months' exposure to tap-water, 101 and 108 respectively; 6 months' exposure to sea-water, 107 and 108; 6 months' alternate wet and dry, 60 and 68; 35 days' exposure to hot water, 116 and 117; and 6 months' exposure to 0·05 per cent. sulphuric acid, 102 and 112. For the observations of H. O. Forrest and co-workers, *vide* the corrosion of iron—**13.** 66, 403. P. Koetzschke found that additions of chromium to nickel cast iron do not materially aid resistance to corrosion in acetic acid because of the unfavourable effect of nickel. H. Ipavic studied the action of hydrogen sulphide; G. H. McGregor and J. W. Stevens, sulphur dioxide; S. M. Norwood, the effect of nitridization; and F. H. Rhodes and co-workers, the corrosive action of phenols. For O. K. Parmiter's observations, *vide supra*, chromium-iron alloys. Some observations were made by W. Ackermann, J. Arnott, C. B. Bellis, E. Blau, P. Bres, A. Brunner, F. F. Chapman, D. G. Clark, J. Cournot and H. Fournier, C. Duisberg, G. M. Enos, J. L. Everhart, O. Föppl and co-workers, H. J. French and W. A. Tucker, J. A. N. Friend and co-workers, Y. S. Gintzburg and co-workers, R. Hanel, W. H. Hatfield, F. F. Hengstenberg, W. Herrmann, W. Hessenbruch and E. Horst, W. Hessenbruch and W. Rohn, L. W. Hostettler, E. Houdremont and P. Schafmeister, W. R. Huey, F. H. Hurren, C. H. M. Jenkins and co-workers, C. M. Johnson, J. F. Kayser, F. F. Khimushin and M. F. Denisoff, P. Kötzschke and E. Piwowarsky, A. Lissner, E. Maass and W. Wiederholt, R. J. McKay, R. S. MacPherran, C. E. MacQuigg, L. Marti, A. Matagrin, J. A. Mathews, P. S. Menough, J. D. Miller, J. L. Miller, W. M. Mitchell, J. H. G. Monypenny, H. Müller, H. Nakamura, F. Orme, A. R. Page and J. H. Partridge, J. A. Parsons and E. Ryder, P. Payson, J. E. Pollock and co-workers, V. and G. Prever, S. H. Rees, J. Rist and co-workers, F. Rittershausen, W. Rosenhain and C. H. M. Jenkins, A. Sanfourche and A. M. Portevin, M. Sauvageot and L. Lauprète, P. Schufmeister and F. K. Naumann, C. A. Scharschu, F. Schmitz, E. H. Schulz and W. Jenge, H. E. Searle and R. Worthington, M. H. Sommer, L. J. Stanbery, B. Strauss and co-workers, J. Strauss, R. Stumper, R. Sutton, Y. Taji, J. G. Thompson, A. Thum, W. W. Triggs, and E. Wellmann. For the observations of J. F. Kayser, W. Guertler and W. Ackermann, N. B. Pilling and D. E. Ackerman, W. Rohn, J. A. Mathews, and M. Ballay, *vide* chromium steels. W. H. Hatfield obtained the results indicated in Table XIX; they show the percentage composition of the metal and the number of grams dissolved by the acid in 24 hrs., at about 15°. B. Jones, and R. Franks studied the effect of nitridization; A. Fry and P. Schafmeister, intercrystalline corrosion; J. Arend and M. Lobe, and J. A. Mathews, the effect of titanium. The addition of a 5 per cent. nickel to 5 per cent. chromium-steel produces an alloy which is almost wholly resistant to nitric acid; the addition of nickel also materially increases its resistance to hydrochloric acid; and the gradual increase in the proportion of nickel also produces a metal which is attacked only slightly by the acid.

E. H. Schulz and W. Jenge found that a steel containing 0·25 per cent. of carbon, 7·0 per cent. of nickel, and 20 per cent. of chromium, is not stable in contact with *chlorine*, *bromine*, or *iodine*, and with boiling 0·5 per cent. *hydrochloric acid*, the loss in weight in grams per sq. metre per hour was 1·79; and nil with acid 1 : 10. E. Deussen found that the Fe-Cr-Ni alloy (70 : 23 : 7) is rapidly attacked by 20 per cent. hydrofluoric acid, and slowly attacked by the 5 per cent. acid at room temp. E. Wellmann observed that the alloys are not attacked by *hypochlorites* if over $\frac{1}{8}$th mol. proportion of chromium is present. The attack preferentially favours spots where there are slag inclusions. H. Gruber studied the action of hydrogen sulphide between 700° and 1000°.

W. Rohn found the corrodibility of some iron-nickel-chromium alloys expressed as loss in grams per sq. dm. with N, not annealed, and A, annealed alloys, using 10 per cent. acids. The first three alloys had also about Mn, 0·4; Si, 0·3; and

C, 0·2; the alloys with 9 to 20 per cent. of iron had 1 per cent. of manganese, and the alloy with 20 : 63 : 15 had Mn, 1, and C, 0·9 :

Fe : Ni : Cr		HNO_3		H_2SO_4		HCl	
		N	A	N	A	N	A
82 : 0·7 : 15	24 hrs. cold	0	0	4·4	5·4	0·78	0·78
	1 hr. hot .	0·007	0·01	19·5	24	16·3	25·5
82 : 2 : 15	24 hrs. cold	0	0	4·7	4·3	0·19	0·30
	1 hr. hot .	0·003	0·403	15·6	14·4	4·5	10·8
71 : 8 : 20	24 hrs. cold	0·001	0·001	0·007	0·003	0·27	0·25
	1 hr. hot .	0·001	0·001	2·62	2·53	1·34	1·55
55 : 20 : 25	24 hrs. cold	0	0	0·12	0·12	1·0	0·12
	1 hr. hot .	0	0	1·8	1·7	19·0	3·4
50 : 35 : 15	24 hrs. cold	0·05	1·5	0·15	0·14	0·26	0·32
	1 hr. hot .	0·03	2·8	0·08	0·15	0·96	0·30
20 : 64 : 15	24 hrs. cold	0·6	0·19	0·1	0·002	0·12	0·14
	1 hr. hot .	0·02	49·2	0·49	0·020	3·24	1·97
20 : 63 : 15	24 hrs. cold	49·2	—	0·1	—	0·3	—
	1 hr. hot .	—	—	0·49	—	0·26	—
20 : 65 : 15	24 hrs. cold	0·065	0·040	0·002	0·006	0·020	0·025
	1 hr. hot .	0·0025	0·0025	0·020	0·015	0·26	0·18
16 : 50 : 33	24 hrs. cold	0	0	0·03	0·02	0·36	0·09
	1 hr. hot .	—	—	0·31	0·01	4·2	3·51
10 : 69 : 20	24 hrs. cold	0·02	0·26	0·14	0·02	1·44	0·08
	1 hr. hot .	0·01	0·28	0·09	0·06	1·66	1·72
9 : 65 : 25	24 hrs. cold	0	0·01	0·03	0·02	0·42	0·13
	1 hr. hot .	0·06	0·02	0·12	0·06	3·84	2·65

Fe : Ni : Cr		CH_3COOH		H_3PO_4	
		N	A	N	A
82 : 0·7 : 15	24 hrs. cold	0	0	0	0
	1 hr. hot .	0·003	0·018	0·003	0·003
82 : 2 : 15	24 hrs. cold	0	0	0	0·003
	1 hr. hot .	0·003	0·003	0·003	0·006
71 : 8 : 20	24 hrs. cold	0	0	0	0
	1 hr. hot .	0·002	0·005	0·003	0·003
55 : 20 : 25	24 hrs. cold	0	0	0	0
	1 hr. hot .	0·005	0·01	0·005	0·015
50 : 35 : 15	24 hrs. cold	0·008	0·012	0·006	0·016
	1 hr. hot .	0·035	0·026	0·1	0·29
20 : 64 : 15	24 hrs. cold	0·012	0·016	0·002	0·008
	1 hr. hot .	0·02	0·01	0·056	0·062
20 : 63 : 15	24 hrs. cold	—	—	—	—
	1 hr. hot .	—	—	—	—
20 : 65 : 15	24 hrs. cold	—	—	—	—
	1 hr. hot .	—	—	—	—
16 : 50 : 33	24 hrs. cold	0	0	0	0
	1 hr. hot .	0	0	0·6	0·011
10 : 69 : 20	24 hrs. cold	0·005	0·005	0·01	0·045
	1 hr. hot .	0·005	0·005	0·11	0·05
9 : 65 : 25	24 hrs. cold	0	0	0·002	0
	1 hr. hot .	0·008	0	0·08	0·16

Another alloy with 2 per cent. manganese, and 5 per cent. of aluminium, gave :

17 : 61 : 15	24 hrs. cold	0·28	0·26	0·07	0·05	0·27	0·26	0·004	0·014	0·06	0·068
	1 hr. hot .	0	0	0·34	0·22	6·7	6·5	0·004	0	0·024	0·016

W. Guertler and W. Ackermann examined the dissolution of homogeneous solid soln. of chromium, nickel, and iron in 1 and 20 per cent. nitric acid, and in 1 per cent. sulphuric acid. The results are roughly in accord with G. Tammann's one-eighth rule. Thus, the rate of dissolution of nickel-iron alloys in nitric acid increases suddenly with 12·5 at. per cent. Ni, and decreases again suddenly at 25 at. per cent. Ni; and chromium-iron alloys become passive when the chromium content exceeds 12·5 at. per cent. In the ternary alloys passivity towards nitric acid is afforded by a similar proportion of chromium, variations in the nickel and iron content having no effect on the behaviour of the alloys. Iron-nickel alloys

TABLE XXII.—THE EFFECT OF ACIDS ON NICKEL-CHROMIUM STEELS.

C	Mn	Ni	Cr	Si	HCl (sp. gr. 1·18)	HNO_3 (sp. gr. 1·20)	H_2SO_4 (sp. gr. 1·118)
0·36	0·18	0·10	5·06	0·05	0·3075	0·8989	0·2198
0·36	0·13	5·42	5·06	0·05	0·1763	0·0003	0·0720
0·35	0·16	10·39	5·13	0·03	0·1897	0·0059	0·1329
0·30	0·14	15·27	4·90	0·07	0·0963	0·0001	0·0015
0·36	0·20	20·02	5·05	0·16	0·0367	0·0002	0·0008
0·29	0·22	0·09	10·06	0·14	0·1492	0·0001	0·2143
0·31	0·36	4·88	9·84	—	0·1732	0·0001	0·0689
0·56	0·21	0·10	12·47	0·12	0·1845	nil	0·2496
0·51	0·17	5·23	11·81	0·12	0·1479	nil	0·1321
1·07	0·44	0·13	12·26	0·09	0·1869	0·0004	0·3565
1·16	0·39	5·33	12·84	0·14	0·1747	0·0001	0·2288
1·07	0·32	10·33	12·04	0·24	0·1843	0·0002	0·1444
0·49	0·21	0·14	19·66	0·29	0·1709	nil	0·3530
0·52	0·31	5·40	18·45	0·29	0·1664	nil	0·2825
0·44	0·31	15·15	19·16	0·33	0·0968	nil	0·0015
1·04	0·21	0·22	20·08	0·14	0·2615	0·0001	0·2904
1·09	0·19	5·44	19·48	0·28	0·2862	nil	0·1311
1·01	0·17	14·90	19·21	0·28	0·0904	nil	0·0016

have a higher resistance to corrosion by sulphuric acid when the nickel exceeds 12·5 at. per cent., whereas chromium-iron alloys dissolve more rapidly when the chromium exceeds 12·5 at. per cent., and most rapidly when it exceeds 25 at. per cent. In the ternary alloys the molecular limit 2/8(Cr+Ni) seems to be of importance especially when the chromium content is high, *e.g.*, 17–18 per cent. Cr and 6 per cent. Ni; this alloy is fairly resistant to attack by 1 per cent. sulphuric acid, whereas alloys containing more than 75 at. per cent. Fe are more readily dissolved than is iron itself. Towards acetic acid and mixtures of hydrochloric acid and hydrogen peroxide excess of chromium above 12·5 at. per cent. induces passivity. The above results indicate that chromium alone has a protective action when an oxidizing agent is present and nickel alone in the absence of an oxidizing agent.

E. H. Schulz and W. Jenge found that with conc. *nitric acid* at 20°; and with the boiling 1 : 1 and conc. acids, the losses were respectively 0·04 and 0·02; with boiling, conc. nitric acid and 5 per cent. sulphuric acid, the loss was 0·59. With 10, 30, 66, and 98 per cent. *sulphuric acid* at 20°, the losses were respectively 0·07, 0·16, 0·001, and 0·012; with boiling 20 per cent. acid, 36·0; with 98 per cent. acid at 100°, 4·68; with 58 per cent. sulphuric acid, 40 per cent. nitric acid, and 2 per cent. water at 20°, 60°, 100°, and 110°, the losses were respectively 0·00, 0·05, 0·7, and 7·6; with 10 per cent. sulphuric acid sat. with copper sulphate, at 20°, nil; with *sulphurous acid* sat. at 20 atm. press., at 180°, 110; with sulphurous acid and 1·0 per cent. sulphuric acid at 10°, 0·05; E. Wellmann found that *hydrogen sulphide* attacks the chromium-nickel steels at 300°, at lower temp. there is a corrosive action, but no sulphide is formed; and *sulphur dioxide* attacks the metal over about 400°. Air and water favour the attack at lower temp. I. Musatti and A. Reggiori studied the subject. J. D. Miller found the ternary alloy one of the best metals to resist attack by *sulphite* liquors. According to E. H. Schulz and W. Jenge, the losses in weight in grams per sq. metre per hour with 1 : 1 and boiling, conc. *acetic acid*, are respectively 0·03, and 0·60; with 1 : 10 and 1 : 1 boiling *formic acid*, respectively 2·48, and 9·3; with boiling 10 and 45 per cent. *phosphoric acid*, respectively 0·01 and 0·04; and with 80 per cent. phosphoric acid, at 110° and 115°, respectively 31·3 and 134·3; A. M. Portevin and A. Sanfourche, F. A. Rohrman, and P. R. Kosting and C. Heins studied the action of phosphoric acid. E. H. Schulz and W. Jenge found that the loss in grams per sq. metre per hour with a sat. soln. of *boric* acid, at 100° is nil; the losses with a sat. soln. of oxalic acid at 20°, 40°, and boiling, are respectively 0·00, 0·01, and 16·5; with a sat. *lactic acid* at 20°, nil; sat. *butyric acid* at 20° and 130°, respectively nil and 0·03; *sebacic acid* at 150°, 0·03; sat. *tartaric acid*, boiling, 7·8; boiling, sat. *gallic acid*, nil; *linseed oil* and 3 per cent. sulphuric acid at 200°, 0·05; raw *carbolic acid*, at 90°, 0·05; 5 per cent. and sat. *citric acid*, boiling, respectively nil, and 2·19. E. Wellmann found that alloys with less than ⅛th mol. proportion of chromium are attacked by soln. of tartaric and nitric acid, but not if more chromium is present. The alloys are not attacked by aq. soln. of *phenol*. H. A. Trebler and co-workers, and W. A. Wesley and co-workers studied the

action of milk. J. G. Thompson and co-workers studied the action of soln. of *urea*, and of *ammonium carbamate*. According to H. Schulz and W. Jenge, with a boiling 10 and 25 per cent. and a sat. soln. of *sodium chloride*, the losses in grams per sq. metre per hour were respectively nil, 0·03, and 0·10; a 1 : 1 soln. of *sodium sulphide*, at 90°, 0·02; a boiling, sat. soln. of *potassium chlorate*, nil; *potassium hypochlorite* at 20° and 105°, respectively 0·01 and 0·53; a boiling, sat. soln. of *potassium hydrotartrate*, 0·09; *ammonium nitrate* at 107°, 0·02; boiling 1 : 1 *copper nitrate*, nil; boiling 1 : 1 *copper sulphate*, nil; boiling 1 : 1 *copper chloride*, 464; 1 : 1 *iron chloride* at 50°, 101; *tin chloride* of sp. gr. 2·13; at 35°, 0·04; an aq. soln. of tin chloride, at 20°, 2·28; *zinc chloride* at 50°, 0·07; *ammonium chlorostannate* at 20°, 0·052; 0·7 per cent. *mercuric chloride* at 20°, and boiling, respectively 0·88 and 3·60; boiling aq. *ammonia*, nil; soln. of *calcium chloride* at 100°, nil; boiling *ammonium chloride*, nil; 20 per cent. *sodium hydroxide* at 110°, 0·02, 34 per cent. at 100°, nil, and *sodium hydroxide* at 318°, 0·22, boiling 27 and 5 per cent. *potassium hydroxide*, respectively nil and 0·40; and *potassium hydroxide* at 360° and 600° respectively, 3·5 and 37·9. J. L. Everhart noted the alloys gave a good resistance to ammonium chloride. M. P. Balfe and H. Phillips, and A. Gansser noted the resistance of the alloys to tanning liquors; and W. A. Wesley and co-workers, to milk. P. W. Bridgman noted the conditions under which *mercury* amalgamates with freshly fractured surfaces of nickel-steel.

D. J. McAdam observed that the simultaneous action of corrosion and fatigue—corrosion-fatigue—causes failure at stresses far below the ordinary endurance limit—*vide* the corrosion of iron. The results of tests with chromium-nickel steels with 17·71 and 5·42 per cent. of nickel are summarized in Fig. 284. The tests in air (fatigue test), and the test while the steel was exposed to the corrosive action of fresh, carbonate water (corrosion-fatigue test) were made with stresses alternating 1450 revs. per minute. The graph shows the relation between the stress at failure and the logarithm of the number of cycles for failure. The static, fatigue, and corrosion-fatigue tests are as follow (for the corrosion, a fresh, carbonate water, and a salt, river-water with about one-third the saline contents of sea-water were used):

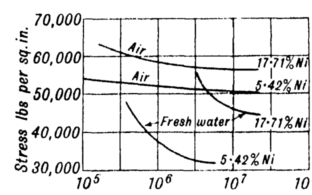


Fig. 284.—The Fatigue and Corrosion-Fatigue Tests of Nickel-Chromium Steels.

Chromium		5·42	10·89	17·32	17·71	20·48
Nickel		22·90	34·70	8·19	25·27	0·25
Tensile strength		93,000	112,300	125,300	115,200	110,900 lbs. per sq. in.
Total elongation		32·3	28·8	45·5	22·5	22·5 per cent. in 2 ins.
Reduction of area		58·6	46·6	53·2	34·9	42·5 per cent.
Endurance limit		50,000	57,000	50,000	54,000	— lbs. per sq. in.
Fatigue-corrosion	Fresh	32,000	41,000	50,000	45,000	48,000 lbs. per sq. in.
	Salt	—	22,000	25,000	34,000	— ,, ,,

J. H. S. Dickenson and W. H. Hatfield studied the **nickel-chromium-beryllium-iron alloys**; M. Wählert and H. Ostermann, and G. d'Ardigny discussed the hardness, and resistance to corrosion of *nimol*, the trade-name of a **copper-chromium-nickel-iron alloy**; and J. S. Vanick and P. D. Merica, the corrosion and heat-resisting qualities of the alloys. W. Kroll investigated the properties of some **nickel-beryllium-chromium steels**, and found for those with about 1 per cent. of beryllium and 20 per cent. of chromium, the Brinell's hardness, with a 1000 kgrm. 10 mm. sphere acting for 1 min.:

Nickel		0	4·13	5·40	6·25	7·33	8·80	9·20 per cent.
Hardness	Quenched 950°	227	279	264	270	286	245	207
	Aged 500°	238	588	494	511	512	367	257
	Annealed 950°	220	—	—	—	—	—	—

and for those with about 6·25 per cent. of nickel, and 1·05 per cent. of beryllium,

Chromium		0·0	9·45	12·69	16·49	20·90 per cent.
Hardness	Quenched 950°	380	373	391	282	270
	Aged 500°	622	663	687	477	511
	Annealed 950°	250	373	350	279	264

The mechanical properties of the alloys with the tensile strength expressed in kgrms. per sq. mm., and Brinell's hardness with a 3000 kgrm. 10 mm. sphere acting for 1 min.,

Cr : Ni : Be	12 : 5 : 1		20 : 7 : 1		20 : 9 : 1		20 : 8 : 1	
	Quenched	Annealed	Quenched	Annealed	Quenched	Annealed	Quenched	Annealed
Tensile strength	130	—	102	—	82	97	80	124
Elongation	7	1	11	1	30	20	28	5 per cent.
Reduction area	47·2	0	7·0	0	66·0	31·0	68·0	8·0
Hardness	350	670	275	480	207	257	—	—
Scleroscope	—	102	—	91	—	54	—	—

The decreases in weight in grams per sq. cm. in 24 hrs. of alloys immersed in different acids were :

Cr : Ni : Be : C	HNO_3 (24·3 per cent.)	HCl (5·36 per cent.)	H_2SO_4 (9·48 per cent.)	CH_3 COOH (80 per cent.)
12 : 5 : 1 : 0	$0{\cdot}0_426$	0·1463	0·1634	$0{\cdot}0_33012$
20 : 7 : 1 : 0	$0{\cdot}0_4163$	0·0142	0·0356	$0{\cdot}0_4286$
20 : 7 : 1 : 0·2	$0{\cdot}0_4000$	0·1117	0·1366	$0{\cdot}0_32884$
12 : 5 : 1 : 0·2	$0{\cdot}0_4600$	0·3689	0·3762	$0{\cdot}0_216374$
14 : 0 : 0 : 0·2	$0{\cdot}0_4117$	0·2424	0·1626	$0{\cdot}0_33566$
20 : 7 : 0 : 0·2	$0{\cdot}0_4071$	0·0760	0·0056	$0{\cdot}0_5426$

V. O. Homerberger and I. N. Zavarine investigated some **nickel-chromium-aluminium-iron alloys** ; J. A. Mathews, A. L. Norbury and E. Morgan, and J. S. Vanick, **nickel-chromium-silicon-iron alloys** ; E. C. Bain and co-workers, **chromium-nickel-iron-titanium alloys** ; and H. Edert, and J. A. Mathews, the mechanical properties of **nickel-chromium-vanadium-iron alloys.**

L. Guillet prepared some **nickel-molybdenum steels** with up to 0·54 per cent. of carbon, 2·96 to 6·40 per cent. of nickel, and 0·51 to 5·13 per cent. of molybdenum. They were all too hard to cut with a saw. The normal steels had the martensitic structure, and only those with high proportions of molybdenum contained carbide. Hence molybdenum favours martensite, and its effect is superadded to that of nickel. Molybdenum, indeed, acts more intensely than tungsten. Quenching at 850° produces no alteration, except that ferrite, when present, disappears ; the carbide, if present, still remains. The martensite has a finer structure after quenching. The fine-grained martensite is difficult to colour on etching ; a prolonged etching with picric acid colours a part more readily than the remainder ; this is the portion in the immediate vicinity of pre-existing grains of carbide, and is probably due to the presence of troostosorbite or some constituent intermediate between martensite and pearlite. If the quenching be carried out at a high enough temp. for all the carbide to dissolve, the differences of colour usually disappear showing that a homogeneous solid soln. is formed. Four hours' annealing between 900° and 1200° does not affect normal steels. The martensite may become more pronounced and coarser, and the grains of carbide better defined, but otherwise no marked change occurs. If the annealed sample be cooled in liquid air, instead of being cooled slowly, steels containing ferrite and martensite become wholly martensitic, and appear as if quenched in liquid air. After case-hardening a ferrite-martensite steel, there remains an unchanged core, then a layer of martensite, and finally an external layer of troostite. The mechanical tests show that the normal steels have a high tensile strength and elastic limit, but the maxima are not attained so long as any ferrite is present. If carbide is present, the tensile strength and elastic limit are lower. The reduction of area and elongation are medium. The resistance to shock is high, particularly with martensitic steels containing a low proportion of carbide. The hardness attains a maximum with the martensitic steels ; as soon as carbide appears, the hardness is reduced, otherwise the proportion of carbon within the above limits has but a slight effect on the hardness. The tensile strength and elastic limit are raised by quenching ; the elongation and reduction of area are reduced, but the former remains fairly high provided carbide is not present. Carbon is prejudicial to the quality of

quenched steel; although it confers great hardness, it makes the steel brittle. Annealing slightly reduces the elongation, reduction of area, and resistance to shock. W. Köster observed that in the ternary system, $FeMo_2$ and NiMo form a continuous series of θ-solid soln. The equilibrium of the eutectic melts, the boundary systems Fe–Mo, and Ni–Mo, and that of the system Fe–Ni, combine to form a four-phase equilibrium: Melt$+\alpha$-solid soln.$=\gamma$-solid soln.$+\theta$-solid soln.; the three-phase area of the α-, γ-, and θ-solid soln. extends from the four-phase stage to ordinary temp. The magnetic transformations were also investigated. R. H. Greaves and J. J. A. Jones found that the temper brittleness of nickel-chromium steels was reduced considerably by the introduction of molybdenum. These steels were studied by K. Sasakawa, B. E. Field, C. McKnight, J. Challansonnet, W. Kahlbaum and co-workers, F. M. Becket, and A. M. Portevin and co-workers. T. S. Fuller found that the thermoelectric force, E millivolts, against copper between 0° and 100° is:

Ni . . .	17	20	55	60	50	55	89·6 per cent.
Cr . . .	4	10	10	15	20	25	5·65 ,,
E . . .	−0·12	−0·46	0	0·07	0·07	−0·08	1·70

B. E. Field studied the resistance of the alloys to corrosion. P. Chévenard found that **nickel-chromium-aluminium steel** had an imperfect reversible transformation between 450° and 800°. C. M. Johnson discussed the **nickel-chromium-silicon steels**; and F. M. Becket and R. Franks, the **nickel-columbium-chromium steels.** J. J. A. Jones, M. R. Chase, G. Mahoux, L. Guillet, J. L. Everhart, G. L. Sakharoff and co-workers, J. H. Andrews, and M. S. Fisher and J. M. Robertson studied the thermal and mechanical properties of the **nickel-chromium-molybdenum steels.** J. H. Binnee studied the solidus and liquidus curves of nickel-chromium-molybdenum steels; and N. P. Inglis and W. Andrews, the effect of hydrogen. M. Sauvageot studied the corrosive action of steam; and A. M. Portevin and co-workers, that of hydrochloric acid. W. Rohn found the corrodibility of the Fe : Ni : Cr : Mo alloys expressed in grams per sq. dm., for N, not annealed, and A, annealed, with 10 per cent. acids. The alloys also had a 2 per cent. manganese, and the 18 : 60·4 : 15 : 4-alloy had 0·57 per cent. of carbon.

Fe : Ni : Cr : Mo		HNO_3		H_2SO_4		HCl	
		N	A	N	A	N	A
19·5 : 61 : 15 : 2·5	24 hrs. cold .	0·018	0·02	0·024	0·04	0·05	0·05
	1 hr. hot .	0·003	0·02	0·027	0·05	0·027	0·03
18 : 61 : 15 : 4	24 hrs. cold .	0·003	0·013	0·015	0·02	0·03	0·043
	1 hr. hot .	0·005	0·005	0·010	0·013	0·037	0·027
18 : 60·4 : 15 : 4	24 hrs. cold .	5·1	0·78	0	0	0	0·58
	1 hr. hot .	—	—	—	—	—	—
20 : 61 : 15 : 4	24 hrs. cold .	0·008	0·011	0·005	0·009	0·07	0·01
	1 hr. hot .	0·025	0·0025	0·025	0·027	0·06	0·02
15 : 61 : 15 : 7	24 hrs. cold .	0·05	0·01	0·06	0·01	0·07	0·01
	1 hr. hot .	0·02	0·0	0·03	0·02	0·06	0·02
15 : 51 : 25 : 7	24 hrs. cold .	0·03	—	0	—	0	—
	1 hr. hot .	0·05	—	0·045	—	0·056	—

Fe : Ni : Cr : Mo		CH_3COOH		H_3PO_4	
		N	A	N	A
19·5 : 61 : 15 : 2·5	24 hrs. cold .	0·008	0·008	0·016	0·005
	1 hr. hot .	0·02	0	0	0·002
18 : 61 : 15 : 4	24 hrs. cold .	0·003	0·008	0·005	0·008
	1 hr. hot .	0·005	0·002	0·002	0·005
18 : 60·4 : 15 : 4	24 hrs. cold .	—	—	—	—
	1 hr. hot .	—	—	—	—
20 : 61 : 15 : 4	24 hrs. cold .	0·008	0·002	0·02	0·012
	1 hr. hot .	0·004	0·006	0·02	0·016
15 : 61 : 15 : 7	24 hrs. cold .	0·008	0·002	0·02	0·012
	1 hr. hot .	0·004	0·006	0·02	0·016
15 : 51 : 25 : 7	24 hrs. cold .	—	—	—	—
	1 hr. hot .	—	—	—	—

These steels were studied by I. Musatti and A. Reggiori, A. Oding, K. Sasakawa, W. Liestmann and C. Salzmann, M. Sauvageot and L. Lauprête, J. J. A. Jones, M. R. Chase, F. F. Khimushin and M. F. Denisoff, G. A. Baker, P. H. Clark and E. L. Robinson, C. C. Hodgson, and H. Korschan studied the **molybdenum-chromium-nickel steels.**

L. Guillet prepared **nickel-tungsten steels** with 0·15 to 0·45 per cent. of carbon, 0·288 to 6·08 per cent. of nickel, and 0·27 to 4·96 per cent. of tungsten. The steels rolled well, but those with the higher proportion of carbon were difficult to machine. The alloys with the smaller proportions of carbon and tungsten contained pearlite, ferrite, and a little martensite; the proportion of martensite increased with the higher proportions of tungsten. The tungsten, indeed, dissolves in the iron aiding the formation of martensite, lowering its transformation point, and when the soln. is saturated, the tungsten separates as carbide. After being quenched from 850°, all the steels gave a very minute, almost invisible, martensite structure. The carbide of tungsten steels disappears after suitable quenching from 850°. Annealing at 900° has no appreciable effect on the structure. After case-hardening, there is a core of ferrite and martensite, then from the centre outwards there is a zone of martensite, a zone of troostosorbite, and finally a zone with polyhedra of γ-iron. If the case-hardening be prolonged, tungsten carbide may be formed. The mechanical tests on the normal steel show that the tensile strength increases slowly with increasing proportions of tungsten; the elastic limit is not affected very much; the elongation and reduction in area vary but little, and they are rather smaller than with nickel-steels; similarly with the resistance to shock. The hardness increases slowly with increasing proportions of tungsten. After quenching, many of the test-pieces were cracked. The effect of quenching from 850° is considerably to raise the tensile strength and elastic limit, and particularly so with steels having a small proportion of tungsten. The elongation remains fairly high, and the reduction in area and resistance to shock are good with steels containing a low percentage of carbon. The hardness is high. Annealing slightly softens these steels. K. Winkler and R. Vogel studied the ternary system. O. Rumschöllel said that tungsten separates out in the freezing of an alloy made by adding iron-tungsten alloy to copper-zinc alloy. The effect of nickel on high-speed steels was studied by V. Ehmke. A. M. Portevin and co-workers studied the corrosive action of hydrochloric acid. M. Sauvageot, and F. F. Khimushin and M. F. Denisoff studied the action of steam, and acids on **nickel-chromium-molybdenum-iron-copper alloys.** F. A. Rohrman studied the action of hydrochloric acid on the **molybdenum-manganese-iron-nickel alloys**; and R. Irmann examined the action of sulphuric acid on **copper-tungsten-iron-nickel alloys**; and he studied their magnetic and electrical properties. J. J. A. Jones, A. M. Portevin and co-workers, W. H. Hatfield, V. Ehmke, W. Haufe, H. J. French and T. G. Digges, L. Guillet, and W. Rosenhain and C. H. M. Jenkins studied the **nickel-chromium-tungsten steels**; and O. Föppl and co-workers, the corrosion of these steels.

N. Parravano, L. Guillet, J. H. Hall, J. J. A. Jones, R. Delbart and E. Lecœuvre, F. F. Khimushin and M. F. Denisoff, and M. M. Romanoff, studied the ternary **nickel-iron-manganese alloys,** and N. Parravano's results are summarized in Fig. 285. Solid soln. are formed in all proportions. The liquidus curves are continuous, and the solidus curves are dotted in the diagram. H. Wedding, T. S. Fuller, R. R. Abbott, J. H. Hall, P. Dejean, H. C. H. Carpenter and co-workers, and J. H. Hall studied the iron-nickel-manganese steels. A. Schulze investigated the conductivity; and G. Watanabe, H. Nakamura, and H. K. Onnes and co-workers, their magnetic properties at a low temp. Y. S. Gintzburg and co-workers, and F. F. Khimushin and M. F. Denisoff studied the corrosion of **manganese-chromium-nickel-iron alloys.** V. Fischer, and N. Parravano also studied the quaternary **nickel-iron-manganese-copper alloys.** R. A. Hadfield, L. Dumas, and H. C. H. Carpenter and co-workers examined some nickel-manganese steels.

L. Guillet examined two series of these steels respectively with 0·15 and 0·75 per cent. of carbon, and each with 2, 12, and 30 per cent. of nickel, and 2, 7, and 15 per cent. of manganese. He found that the constituents of the normal nickel-manganese steels can be represented by Fig. 286. The equation of the P-plane, representing the percentages of the different elements by their chemical symbols, is $\frac{1}{13}\mathrm{Ni}+\frac{1}{6}\mathrm{Mn}+\frac{1}{1\cdot65}\mathrm{C}=1$; and that of the P'-plane, by $\frac{1}{29}\mathrm{Ni}+\frac{1}{13\cdot5}\mathrm{Mn}+\frac{1}{1\cdot65}\mathrm{C}=1$. The solid angle made by the P-plane and O corresponds with the pearlitic steels; the space between the P- and P'-planes, the martensitic steels; and the space in front of the P' plane, with polyhedra of γ-iron. If p denotes the first term of the first equation, and p' the first term in the second equation, then for a pearlitic steel, $p<O$; for a martensitic steel, $p>O$ and $p'<O$; while a steel with polyhedra of γ-iron has $p'>O$. Thus, with C=0·2, Ni=2, and Mn=5, $p>O$, and $p'<O$, so that the steel is martensitic with C=0·2, Ni=30, and Mn=15, $p'>O$, and the steel consists of polyhedra of γ-iron. Steels with values of p and p' approaching zero are near the plane separating two zones, and may contain two kinds of constituents. A steel containing γ-iron, even when bordering closely on the martensitic group, may have in the interior polyhedra of γ-iron, and the exterior surfaces may be all martensitic. A pearlitic nickel-manganese steel undergoes the same transformations as an ordinary steel, but the temp. at which these transformations occur fall as the sum of the nickel, manganese, and carbon rises. On quenching, the martensitic steels usually remain martensitic, and those approaching the γ-iron series have a tendency to develop the polyhedral structure. The γ-iron steels undergo no general alteration on quenching, but the steels with the smallest proportions of carbon and nickel become martensitic, and those which follow undergo only a development or accentuation of the cleavage planes of the polyhedra. The martensite produced in steels with a low percentage of carbon, by the transformation of γ-iron, is of a minute structure, whereas with steels containing a high proportion of carbon, needles consisting of troosto-sorbite are formed. Steels normally exhibiting these needles are transformed into ordinary martensite at 900°. Steels with γ-iron, near the bordering plane, are transformed by a prolonged annealing at a temp. which should be higher in proportion as they are distant from the boundary P'-plane. Those with low percentages of carbon yield fine-textured martensite; and steels with a high proportion of carbon yield well-defined needles. Sometimes only the cleavage planes of the polyhedra are intensified. As in the case of nickel, and manganese steels, when the nickel-manganese steels containing γ-iron and bordering on the martensite group are stressed, the γ-iron is transformed into martensite; and this transformation is the more pronounced the greater are the stresses. The transformation in steels containing much carbon proceeds in two stages: (i) the cleavage planes become more decided; and (ii) needles of martensite are formed. The influence of cooling is similar to that which occurs with manganese and nickel steels. Observations were also made by J. J. A. Jones, N. Parravano, and M. A. Hunter and F. A. Sebast.

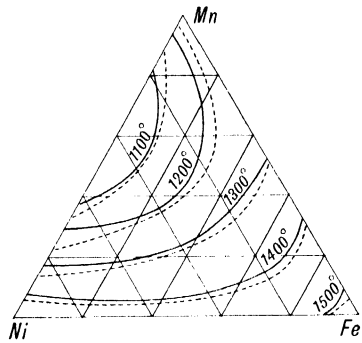


FIG. 285.—The Ternary System: Fe–Ni–Mn.

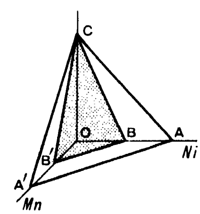


FIG. 286.—Constitution Nickel-Manganese Steels.

W. Brown gave for the sp. vol. of steel with about 0·7 per cent. of carbon, 5·04 per cent. of manganese, and 14·55, 19·00, and 25·00 per cent. of nickel respectively 0·12776, 0·12732, and 0·12642, and for the sp. gr. respectively 7·8272, 7·8542, and 7·910. The mechanical properties of the normalized steels correspond

closely with the structure; and on quenching, the steels containing γ-iron are softened, but the resistance to shock is not always increased. The martensitic steels remain martensitic, but have their tensile strength and hardness increased, and their elongation and reduction of area diminished. Quenching transforms pearlitic steels into martensitic steel, and thus raises their tensile strength, elastic limit, brittleness, and hardness, and lowers their elongation and reduction of area. Steels on the border of the martensitic steels and of the γ-iron steels are softened by quenching if in the normalized state they contain martensite and γ-iron, and are hardened on quenching if, under the same conditions, they contain γ-iron alone. The hardness of the annealed steels corresponds with the production of martensite. G. Klein studied the properties of these alloys. W. Brown found the sp. hts. of the three steels just indicated were respectively 0·1208, 0·1194, and 0·1186. T. S. Fuller found that the thermoelectric force, E millivolts, against copper between 0° and 100° for iron-nickel-manganese alloys, is:

Ni . .	10	12	17	17	17·5	22	44 per cent.
Mn .	3	2	2	3	6	2	6 ,,
E . .	−1·09	−1·02	−1·50	−0·79	−0·73	−1·84	−0·59

M. Maclean found that with wires of *reostene* (Fe, 79·95; Ni, 16·53; Mn, 1·21; Si, 0·61), the e.m.f. of the thermocouple, having one wire permanently stretched longitudinally, was 0·0208 microvolt per degree, when the current passed from the unstretched to the stretched wire; he found:

Load	250	500	750	1000	1250	1500	1750 grms.
Temporary elongation .	0·037	0·085	0·152	0·220	0·257	0·318	0·417 per cent.
Permanent elongation .	—	—	0·037	0·073	0·104	0·134	0·201 ,,
Microvolts per degree .	0·1163	0·1528	0·1528	0·1557	0·1614	0·1717	0·1963

J. G. Gray studied the magnetic properties; H. C. H. Carpenter and co-workers, the corrodibility of the manganese-nickel steels. P. Hidnert and W. T. Sweeney, the thermal expansion of a Ni-Fe-Mn-Cu-Sn-Si (61 : 3·5 : 0·75 : 25 : 9 : 0·75) alloy —so-called M-M-M-alloy.

T. Fleitmann[25] found that **nickel-cobalt alloys** are readily formed and that they can be mixed with 10 per cent. of zinc, cadmium, tin, lead, manganese, or iron without losing their working qualities. H. J. Blikslager, G. Bruni and M. Amadori, A. N. Campbell and F. C. Garrow, T. Fearn, C. G. Fink and K. H. Lah, C. G. Fink and F. A. Rohrman, F. Förster, S. Glasstone, S. Glasstone and J. C. Speakman, E. Haynes, C. Langbein, C. P. Madsen, K. Masaki, W. Pfanhauser, S. A. Pleteneff and V. V. Kusnezova, J. E. Root, H. W. Toepffer, and O. P. Watts discussed the electrodeposition of alloys of the two metals. W. Guertler and G. Tammann studied the f.p. diagram, and the results are summarized in Fig. 287. W. Guertler and G. Tammann, O. Bloch, M. Waehlert, R. Ruer and K. Kaneko, J. A. M. van Liempt, W. Broniewsky and W. Pietrek, and H. Masumoto all agree that a continuous series of solid soln. is formed.

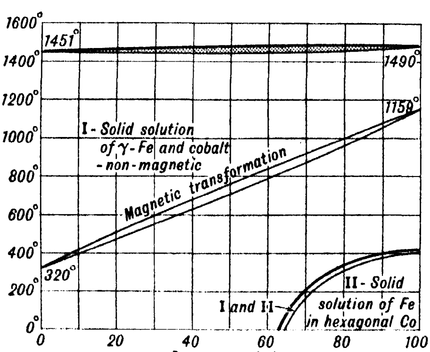


FIG. 287.—Freezing-point Curve of Nickel-Cobalt Alloys.

The composition of the solid soln. which separates and that of the mother-liquor is approximately the same. The f.p. curve separates the field of the molten mass from the non-magnetic solid soln., and the transition curve separates the field of the non-magnetic from the magnetic solid soln. With over 60 per cent. of cobalt,

the solid soln. forms either a close-packed, hexagonal lattice, or the face-centred, cubic lattice or a mixture of the two. A. Schulze thought that the electrical conductivity curves corresponded with the existence of **nickel tetritacobaltide,** Ni_4Co; **nickel hemi-tricobaltide,** Ni_2Co_3; and **nickel tetracobaltide,** $NiCo_4$; and the breaks in the thermal expansion curves to the compounds Ni_4Co, $NiCo_4$, and **nickel cobaltide,** NiCo.

A. Osawa measured the effect of nickel on the lattice constants and found that a=3·508+0·00017143[Co], where [Co] represents the percentage of cobalt, so that the lattice constant of γ-cobalt at room temp. is 3·525 A.; and

Nickel . .	100	90	80	60	40	25	20	10	0 per cent.
a (face-centred)	3·508	3·510	3·509	3·515	3·518	3·521	3·522	3·532	3·525 A.
a (Hexagonal)	—	—	—	—	—	—	2·492	2·492	2·492 A.
c (Hexagonal)	—	—	—	—	—	—	4·036	4·046	4·056 A.

The subject was studied by A. O. Jung, and J. H. Long and co-workers; and the lattice distortion, by V. G. Mooradian and J. T. Norton.

O. Bloch found the sp. gr. to be:

Nickel . .	100	91·22	81·39	69·65	50·69 per cent.
Sp. gr. . .	8·790	8·799	8·872	8·716	8·789
Nickel . .	39·57	30·23	20·46	10·73	0 per cent.
Sp. gr. . .	8·716	8·768	8·755	8·870	8·920

M. Waehlert found Brinell's hardness of the nickel-cobalt alloys to be:

Nickel .	100	90	80	70	60	50	40	30	20	10 per cent.
Hardness .	56	63	65	65	65	65	66	97	149	158

T. Kase, and R. Ruer and K. Kaneko also measured the hardness of these alloys and observed an abrupt change in the curve. H. Masumoto and S. Nara found the coeff. of thermal expansion, α, between 30° and 100°, to be:

Cobalt .	0	10	20	30	40	50	60	70	80	100 per cent.
$\alpha\times10^5$.	1·358	1·345	1·340	1·263	1·250	1·321	1·349	1·256	1·268	1·279

The results plotted in Figs. 288 and 289 show a slow decrease, as up to 30 per cent. of nickel is added to the cobalt; there is an increase to a maximum with about 40 per cent. nickel, and then a decrease to a minimum with about 65 per cent. nickel. After that there is a slow increase up to the value for nickel alone. Observations were made by A. Schulze. The continuous line, Fig. 288, represents the results of H. Masumoto and S. Nara and the dotted line those of A. Schulze. H. Masumoto found a break with 70 per cent. of cobalt.

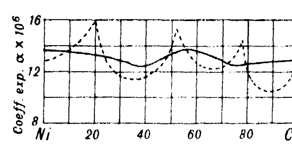


FIG. 288.—The Coefficients of Thermal Expansion of the Cobalt-Nickel Alloys.

H. Masumoto obtained for the thermal conductivity, k cals. per cm. per second, and for the sp. electrical resistance, $R\times10^{-5}$ ohm per cm. cube,

Cobalt . .	0	10	20	30	40 per cent.
k . . .	0·1821	0·1317	0·1228	0·1174	0·1189
R . . .	0·858	1·257	1·392	1·419	1·304
kR . . .	0·156	0·166	0·171	0·167	0·166
Cobalt . .	50	60	70	80	100 per cent.
k . . .	0·1212	0·1253	0·1334	0·1328	0·1299
R . . .	1·373	1·333	1·233	1·206	1·183
kR . . .	0·166	0·167	0·164	0·160	0·154

The results are plotted in Fig. 289. The two conductivities of cobalt decrease with the addition of nickel, and after passing through a minimum with 10 per cent. of nickel, gradually increase, reaching a maximum with 25 per cent. of nickel, after which they decrease and reach a minimum with 70 per cent. of nickel. Above

this minimum, they increase at first gradually, and then rapidly. The maximum conductivities at about 25 per cent. nickel lie near the concentration at which the lattice-change occurs; and the minimum at 10 and 70 per cent. of nickel is a common property of alloys which form a continuous solid soln. The product kR is nearly constant, but decreases slightly with increasing conductivity as in the case of aluminium and the iron-carbon alloys. The electrical resistance was also studied by A. Schulze. R. Ruer and K. Kaneko did not find a break on the electrical resistance curve at 30 per cent. nickel. P. Günther and I. N. Stransky studied the X-ray spectrum. W. Rohn studied the thermoelectric force of the alloys against platinum. H. Masumoto measured the intensity of magnetization of nickel-cobalt alloys with different field-strengths, H, and found:

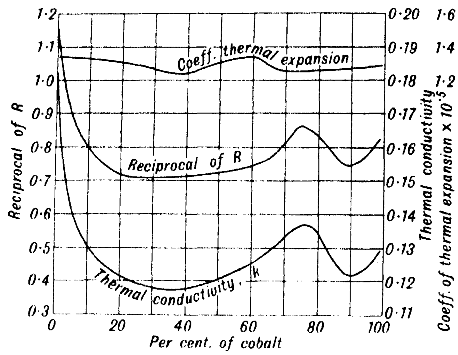


FIG. 289.—The Thermal and Electrical Conductivities of the Nickel-Cobalt Alloys.

Co							
0 per cent.	H	2·5	43·2	96·3	204	423	642
	I	98·1	384	438	484	501	506
10 per cent.	H	1·6	42·8	96·4	205	424	643
	I	169	522	573	599	620	622
20 per cent.	H	2·0	39·4	22·4	201	419	638
	I	136	598	663	699	718	722
40 per cent.	H	3·3	37·5	112·8	192	409	627
	I	66·1	531	737	814	883	901
60 per cent.	H	4·8	44·2	119·5	199	414	632
	I	27·1	434	713	828	974	1032
80 per cent.	H	4·7	42·7	116·3	195	410	627
	I	29·4	484	829	964	1116	1181
100 per cent.	H	5·3	38·7	101·6	207	421	637
	I	8·4	105·0	347	547	750	878

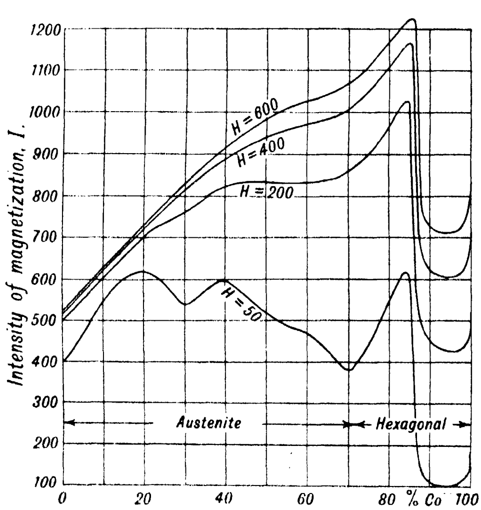


FIG. 290.—The Intensity of Magnetization of the Cobalt-Nickel Alloys.

The results are plotted in Figs. 290 and 291. The numbers in Fig. 291 refer to the strength of the magnetic field in gauss; and in Fig. 290, the nature of the main constituent is indicated. The magnetization of the cobalt-nickel alloys is easy where they have the γ-solid soln., but where they have the close-packed, hexagonal lattice, it is difficult. The addition of cobalt to nickel thus makes the magnetism more difficult. There is a minimum near where H=50 for 30 per cent. nickel, and this minimum becomes less marked as the magnetic field increases. The minimum represents the point where the lattice changes from the close-packed hexagonal to the face-centred cubic. Observations were also made by S. J. Barnett and L. J. H. Barnett, O. Bloch, W. Broniewsky and W. Pietrek, P. Chévenard, G. W. Elmen, R. Forrer, E. Freese, K. Honda,

S. Kaya and A. Kussmann, L. W. McKeehan, K. Lewkonja, L. Néel, G. Tammann, and P. Weiss and co-workers. P. Weiss and R. Forrer's results for the saturation capacity of the nickel-cobalt alloys are summarized in Fig. 292. Alloys with 68 to 100 per cent. of cobalt are stable, and have

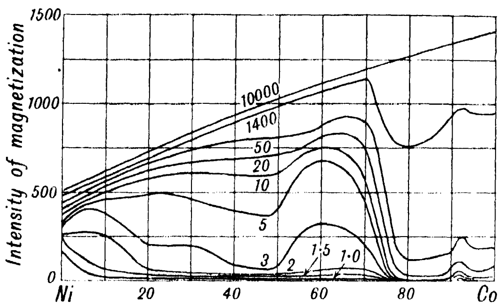


FIG. 291.—The Intensity of Magnetization of the Cobalt-Nickel Alloys.

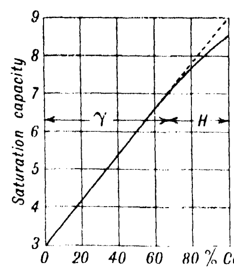


FIG. 292.—Saturation Capacity of the Nickel-Cobalt Alloys.

a hexagonal lattice—H-nickel-cobalts—and those with less cobalt have a face-centred cubic lattice—γ-nickel-cobalts. According to O. Bloch, the magnetic susceptibility, $\chi\times10^{-6}$ mass unit, of the alloys at different temp. furnish linear curves :

per cent. Ni								
90		614°	668°	795°	896°	1004°	1106°	1287°
	$\chi\times10^6$.	70·50	45·71	24·34	17·99	12·96	11·74	9·95
80		699°	751°	875°	964°	1068°	1169°	1261°
	$\chi\times10^6$.	102·00	61·81	31·47	23·13	18·23	14·63	12·61
70		763°	769°	860°	904°	1081°	1228°	1280°
	$\chi\times10^6$.	138·9	121·2	56·02	43·60	23·60	17·40	15·50
60		861°	878°	930°	1007°	1075°	1172°	1238°
	$\chi\times10^6$.	163·9	121·2	81·7	50·56	37·78	28·22	24·10
50		805°	930°	953°	1001°	1150°	1173°	1265°
	$\chi\times10^6$.	363·6	243·9	140·8	98·0	70·20	41·00	31·10
40		1013°	1048°	1071°	1104°	1191°	1234°	1237°
	$\chi\times10^6$.	203·2	136·0	113·0	88·2	56·02	46·00	45·57
30		1032°	1066°	1109°	1147°	1199°	1252°	1293°
	$\chi\times10^6$.	370·4	200·0	119·8	99·1	70·51	52·77	47·52
20		1085°	1102°	1140°	1176°	1202°	1233°	1275°
	$\chi\times10^6$.	367·5	296·0	178·5	126·3	105·8	86·6	71·4
10		1148°	1150°	1194°	1203°	1231°	1271°	1299°
	$\chi\times10^6$.	344·8	285·7	186·9	158·7	123·1	100·1	86·2

The Curie point, or the transformation temp. of the alloys, is :

Cobalt . .	1·3	9·5	18·0	30·3	59·8	69·1	79·5	90·5	98·2 per cent.
Curie point .	315°	455°	522°	669°	876°	946°	982°	1084°	1137°

The Curie points and the saturation values, $B-H=4\pi I\alpha$, both increase as the percentage of cobalt increases, Fig. 293. R. Ruer and K. Kaneko, W. Guertler and G. Tammann, O. Bloch, and P. Weiss studied the effect of temp. ; Y. Masiyama, L. W. McKeehan, and P. P. Cioffi, the magnetostriction ; J. Cournot, the non-magnetic alloys of nickel and cobalt ; and R. Forrer, the magnetic moment of the alloys. The measurements of H. Masumoto on the magnetostriction of the cobalt-nickel alloys are summarized in Fig. 294. P. Weiss and co-workers measured the saturation magnetization at temp. down to that of liquid air. Y. Dorfman studied the magnetic moments. J. H. Long and co-workers, and H. Remy and H. Gönningen studied the contact catalyses of the $2H_2+O_2$ reaction by the alloy. M. Waehlert found that with the nickel-cobalt alloys, the losses in

weight, mgrms. per sq. cm.—during the time stated in brackets—for sulphuric acid and nitric acids—are :

Cobalt		10	20	40	50	60 per cent.
Conc. of acid per cent.—						
H_2SO_4	1 (48)	—	—	—	—	—
	5 (24)	0·60	0·34	0·34	1·675	2·70
	10 (24)	0·25	0·17	0·17	0·34	0·34
	20 (24)	0·25	0·25	—	0·25	0·25
	50 (24)	0·08	0·08	—	0·08	0·08
HNO_3	1 (24)	—	0·18	15·60	—	25·60
	5 (24)	—	6·87	24·80	—	69·90
	10 (24)	—	13·50	—	—	—
	20 (24)	—	8·15	—	—	—

W. Guertler and T. Liepus found that the 50 : 50 Ni : Co alloy is stable after 24 hrs.' exposure to 10 and 50 per cent. nitric acid, 10 and 36 per cent. hydrochloric acid, and aqua regia ; it is stable for less than 8 hrs. in 10 per cent. sulphuric

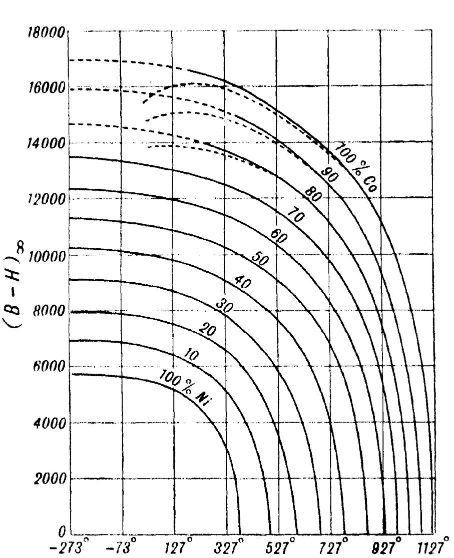


FIG. 293.—The Effect of Different Magnetic Field on the Curie Points of the Cobalt-Nickel Alloys.

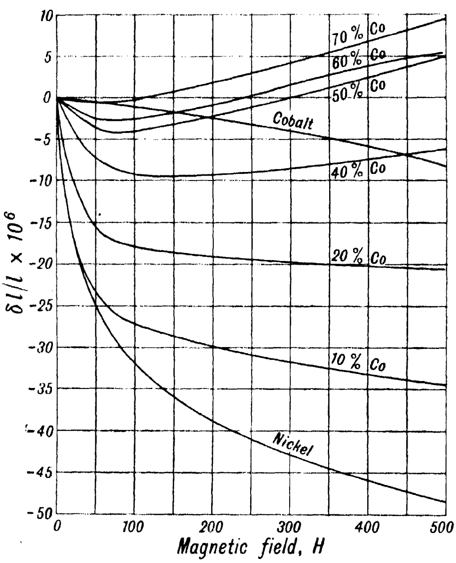


FIG. 294.—The Magnetostriction of the Cobalt-Nickel Alloys.

acid, 20 per cent. sulphuric acid sat. with sodium sulphate, acetic acid, citric acid, tartaric acid, 10, 50, and 70 per cent. aq. ammonia, chlorine water, sea-water, rain-water, magnesium chloride soln., and 10 and 50 per cent. sodium hydroxide ; it is stable for 24 hrs. in 10 per cent. sodium sulphide, and less than 8 hrs. in a 50 per cent. soln. ; whilst it is stable 8 hrs. in a soln. of sodium sulphide (4 per cent.) and alkali (8 per cent.). The nickel-cobalt alloys with 30 to 56 per cent. of molybdenum become more and more stable in these soln. They also examined the corrodibility of the nickel-cobalt-chromium-molybdenum alloys. M. Jungek studied the alloys with carbon.

M. Waehlert found that the ternary **nickel-cobalt-copper alloys** form solid soln. The Brinell's hardness of the ternary alloys is indicated in Table XXIII. The limits of flow—die Fliessgrenze—in kgrms. per sq. mm., and the ratio of Brinell's hardness and the limits of flow, are as follow :

Cu : Ni : Co	80 : 10 : 10	60 : 20 : 20	40 : 50 : 10	40 : 30 : 30
Flow	24·00	32·40	18·00	39·60
Ratio	5·80	5·50	7·12	5·50
Cu : Ni : Co	40 : 10 : 50	70 : 20 : 10	100 : 0 : 0	90 : 10 : 0
Flow	24·30	22·00	5·90	8·10
Ratio	6·20	5·18	5·41	5·55

TABLE XXIII.—BRINELL'S HARDNESS AND RESISTANCE TO CORROSION OF THE COBALT-NICKEL-COPPER ALLOYS.

Cu-Ni-Co	Brinell's hardness	Per cent. nitric acid						Per cent. sulphuric acid						
		1 (48)	5 (24)	10 (24)	20 (24)	30 (24)	50 (24)	1 (72)	5 (24)	10 (24)	20 (24)	30 (24)	50 (24)	100 (24)
100–0–0	28	0·51	0·67	0·25	10·50	380	—	—	0·17	0·25	0·08	0·17	0·08	—
80–20–0	45	0·42	3·35	13·30	16·40	92·50	—	—	0·17	0·80	—	—	—	—
80–10–10	149	7·00	11·00	14·30	39·60	—	—	0·95	0·17	0·25	0·17	0·17	0·17	0·08
70–30–0	57	0·36	2·10	3·65	4·60	16·30	693·5	0·25	0·17	0·42	—	—	—	—
70–20–10	114	—	—	—	—	—	—	—	—	—	—	—	—	—
70–10–20	120	2·56	60·30	—	—	—	—	0·69	0·17	0·25	0·17	0·17	0·17	0·08
60–40–0	61	0·42	2·10	4·00	1·20	1·17	46·20	—	0·08	0·60	0·07	0·07	0·07	—
60–30–10	118	0·67	2·60	8·00	1·50	0·50	95·00	0·92	0·17	0·08	0·08	0·08	0·08	—
60–20–20	178	28·00	16·00	—	—	—	—	0·20	0·25	0·34	—	—	—	—
60–10–30	124	2·90	72·30	—	—	—	—	0·33	0·17	0·17	0·17	0·17	0·17	0·08
50–50–0	64	0·60	0·95	1·78	0·51	0·34	19·50	—	—	1·10	—	—	—	—
50–40–10	122	—	3·25	3·50	0·08	—	10·80	1·33	0·08	1·00	—	—	—	—
50–30–20	205	0·58	2·00	5·35	27·70	—	—	1·00	0·25	0·22	—	—	—	—
50–20–30	179	12·00	115·60	—	—	—	—	0·67	0·25	0·22	—	—	—	—
50–10–40	140	13·00	161·00	—	—	—	—	—	—	—	—	—	—	—
40–60–0	66	0·68	0·84	1·30	0·34	0·34	7·93	—	0·17	0·85	—	—	—	—
40–50–10	128	0·58	0·51	1·60	0·58	0·25	8·75	0·25	0·17	0·25	0·17	—	—	—
40–40–20	202	0·68	1·02	6·60	5·10	1·40	18·30	0·76	0·34	0·22	0·17	0·08	—	—
40–30–30	218	12·00	5·85	26·50	24·00	—	—	0·92	0·33	0·17	—	—	—	—
40–20–40	180	17·00	171·50	—	—	—	—	0·34	0·50	0·25	0·18	0·08	—	—
40–10–50	151	—	—	—	—	—	—	—	—	0·25	0·17	—	—	—
30–70–0	70	—	—	—	—	—	—	0·51	0·25	0·42	—	—	—	—
30–60–10	87	—	—	—	—	—	—	—	—	—	—	—	—	—
30–50–20	137	0·67	0·08	1·00	0·42	0·34	6·20	—	0·17	0·34	—	—	—	—
30–40–30	178	0·95	2·75	9·60	12·50	5·00	15·30	1·00	0·35	0·35	0·08	0·08	0·08	—
30–30–40	184	11·10	145·70	—	—	—	—	1·10	0·08	1·25	1·10	0·42	0·17	—
30–20–50	181	4·10	176·50	—	—	—	—	0·50	0·34	0·25	0·17	0·17	0·07	—
30–10–60	156	27·80	113·40	—	—	—	—	0·43	0·34	0·17	0·25	0·17	0·08	—
20–80–0	74	—	—	—	—	—	—	—	—	—	—	—	—	—
20–70–10	75	—	—	—	—	—	—	—	—	—	—	—	—	—
20–50–30	78	—	—	—	—	—	—	—	—	—	—	—	—	—
20–40–40	176	—	—	—	—	—	—	—	—	—	—	—	—	—
10–90–0	67	—	—	—	—	—	—	—	—	—	—	—	—	—
10–80–10	77	—	—	—	—	—	—	—	—	—	—	—	—	—
10–70–20	80	—	—	—	—	—	—	—	—	—	—	—	—	—

showing that the limit of flow is proportional to Brinell's hardness. The losses in weight in mgrms. per sq. cm. of surface in nitric and sulphuric acids are indicated in Table XXIII. The time of the exposure in hours is indicated in brackets. Many of the Ni-Co-Cu alloys are mechanically superior to monel metal. Thus, the 30 : 30 : 40-alloy is comparable in strength to a 0·7 per cent. carbon steel, and the 20 : 20 : 60-alloy is comparable with a 0·6 per cent. carbon steel, and it can be compressed twice as much as the other ternary alloy. The elastic limit is about twice that of monel metal, and the alloys can be worked better mechanically. Many of the alloys are harder than monel metal. The m.p. of the alloys are indicated in Fig. 295. The ternary alloys are all less resistant towards acids than is monel metal, but some are nearly as resistant, and should be preferred whenever greater hardness, greater strength, and better working properties are desired. The alloys are not much attacked by 20 per cent. or more conc. sulphuric acid, but they are attacked by nitric acid. M. Waehlert and co-workers studied the corrodibility of the **copper-chromium-nickel-iron alloys**—called commercially *nimol*—and of the **copper-cobalt-nickel alloys,** and J. F. Dillinger and M. Bozorth, their magnetic properties.

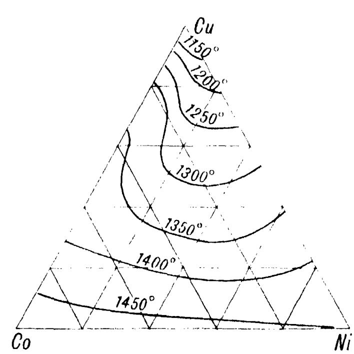


FIG. 295.—Fusion Curves of the Ternary System : Ni–Co–Cu.

Some complex alloys Cu-Ni-Co-Zn, and Cu-Ni-Co-Pb, were discussed by C. Bischoff; Cu-Ni-Co-Fe-Mg (44 : 20 : 3 : 7 : 25) by C. Parnacott; C. L. Clark

and A. E. White, the **titanium-nickel-cobalt alloys**; N. Parravano and C. Mazzetti, the **lead-nickel-cobalt alloys**; W. Guertler, and W. Guertler and T. Liepus, the **chromium-cobalt-nickel alloys,** and the **molybdenum-cobalt-nickel alloys.** The General Electric Co. patented a **nickel-cobalt-manganese alloy**—about 75 : 25 : 2—obtained by melting the cobalt and nickel in an alundum crucible in an atm. of hydrogen, and adding manganese at about 1250° and chilling the product in water. The subject was studied by K. Honda and co-workers. J. Obata discussed the effect of a magnetic field on the electrical resistance of some of the **nickel-iron-chromium-manganese alloys.** W. S. Smith and co-workers, and W. Guertler and G. Tammann discussed the ternary **nickel-cobalt-iron alloys**; the results are due to T. Kase. Measurements were also made by A. Osawa. C. R. Austin and G. P. Halliwell studied the mechanical properties at a high temp. P. H. Brace found that the addition of cobalt to the iron-nickel alloys, say invar, reduces the thermal expansion. The subject was investigated by H. Scott, who found that the effect is limited by the Ar_3-transformation at about −100°. With the ternary alloys containing the permissible maximum amount of cobalt, the addition of manganese is detrimental, and of carbon beneficial. The effect of carbon is indirect, in that its effect on the Ar_3-arrest allows the rise of a higher proportion of cobalt than is otherwise permissible. In the case of invar, the addition of cobalt lowers the coeff. of expansion by about $0{\cdot}5 \times 10^{-6}$ per degree. H. Masumoto measured the coeff. of thermal expansion of the ternary alloys between 30° and 100°, and the results $\times 10^6$ are summarized in Fig. 296. The minimum at 18 per cent. and the maximum at 25 per cent. nickel found on the curves for the nickel-iron system, diminish first rapidly and then gradually as cobalt is added to the system, and they disappear when 40 per cent. of cobalt has been added. The small coeff. of expansion of invar, with 36·5 per cent. of nickel, rapidly decreases as cobalt is added to the alloy, and reaches a minimum with 5 per cent. of cobalt, and afterwards rapidly increases. The addition of manganese to the ternary alloys lowers the temp. of the A_3-transformation. The alloys were discussed by H. Kühlewein, and the thermal expansion of the alloys by H. Scott. B. V. Hill measured the sp. ht. of **nickel-cobalt-iron-manganese alloys.**

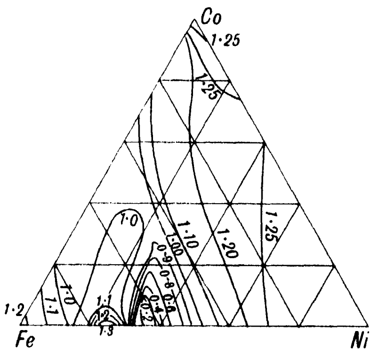


FIG. 296.—The Thermal Expansion Coefficients of the Co-Ni-Fe Alloys.

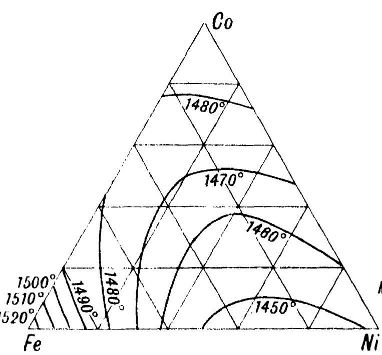


FIG. 297.—The Liquidus Curves of the Nickel-Cobalt-Iron System.

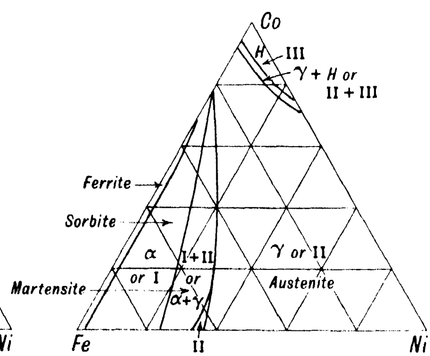


FIG. 298.—Equilibrium Diagram of the Nickel-Cobalt-Iron System.

K. Honda and co-workers studied the properties of magnetic **nickel-cobalt-iron-titanium alloys.**

T. Kase prepared the nickel-cobalt-iron alloys and obtained the isothermal liquidus curves shown in Fig. 297. There exists neither a ternary eutectic nor a compound; but after complete solidification a continuous γ-solid soln. of these metals is formed, although it changes on further cooling. The lowest point in the isothermal liquidus curves corresponds with about 70 per cent. of nickel at 1437°, and the surface ascends gradually towards the iron and cobalt sides so that it is a little concave above. In the completely solidified alloys, on the iron and cobalt sides, there is an allotropic change $\gamma \rightleftharpoons \alpha$, Fig. 298. The beginning and ending surfaces of the transformation are lowered from the A_3-point in the binary system to the temp. of liquid air as the nickel content increases. The A_2-surface which passes through the transformation points of cobalt, 1115°, and nickel, 345°, is convex above. On the iron side, another surface of the A_2-formation exists which coincides with the surface of the A_2-transformation on adding a small quantity of nickel and cobalt to the iron. Both with the binary and ternary alloys the effect of cobalt on the A_3-point in iron is to raise it, and the effect of nickel is to lower it. The alloys were studied by C. R. Austin and G. P. Halliwell, P. P. Cioffi, and W. S. Smith and co-workers. The X-radiograms, indicated in Fig. 298, are by T. Kase, and H. Masumoto, show a narrow region of ferrite; then the α-solid soln. of sorbite; the $\alpha+\gamma$ solid soln. or martensite; the γ-solid soln. or austenite; the H solid soln. which has a hexagonal close-packed lattice; the region of the $\gamma+H$ solid soln. The isothermal lines of the transformation surfaces are shown in Fig. 300.

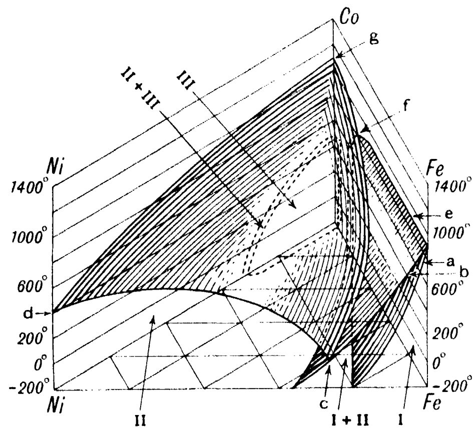


FIG. 299.—The Allotropic Forms of the Iron-Cobalt-Nickel Alloys.

The allotropic forms of the iron-cobalt-nickel alloys are indicated in Fig. 299, due to T. Kase—*confer* the diagrams for the binary systems. The iron corner

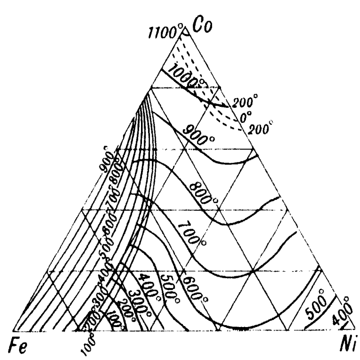


FIG. 300.—The Isothermals of the Transformation Surfaces of the Nickel-Cobalt-Iron Alloys.

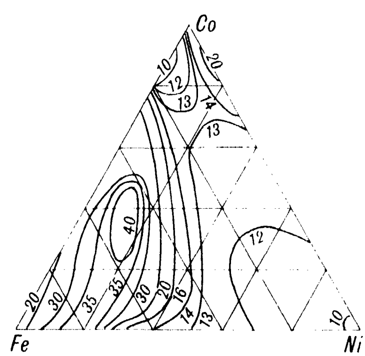


FIG. 301.—The Scleroscopic Hardness of the Nickel-Cobalt-Iron Alloys.

furnishes homogeneous solid soln. of α-iron, nickel, and cobalt having a body-centred cubic lattice—α-iron, region I, Fig. 298. This furnishes a heterogeneous mixture, region I and II consisting of soln. I with α-iron, and a solid soln. with

γ-cobalt and γ-iron. Region II has a continuous series of homogeneous solid soln. of nickel, γ-iron, and γ-cobalt. Near the cobalt apex, there is region III having solid soln. of iron and nickel in hexagonal cobalt. There is an intermediate region with a mixture of solid soln. II and III. The limit of the region II is bounded by the region of magnetic transformation. The A_2-transformation curve begins in the γ-region of the three binary systems and forms a small surface *abe*, Fig. 299, bounded by the A_3-transformation curve. In this region, the α-structure passes

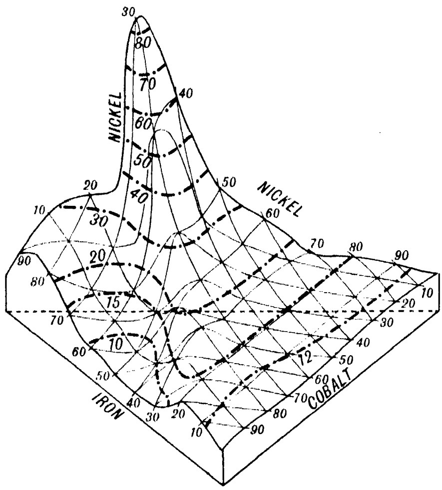


FIG. 302.—Electrical Resistances of the Fe-Co-Ni Alloys.

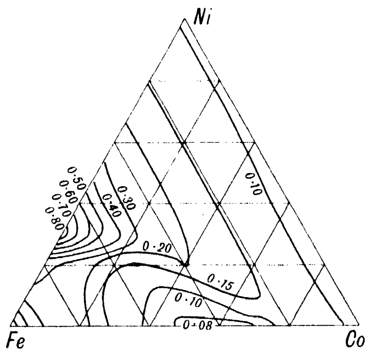


FIG. 303.—The Electrical Resistance, $R \times 10^4$ ohm, of the Ternary Alloys.

into the γ-structure, and the magnetic alloy with a body-centred cubic lattice passes into a non-magnetic alloy with a face-centred cubic lattice. The region of magnetic transformation is accordingly bounded by *abcdefg*, that is, by the A_2-transformation surface *abc*; by the A_3-surface, *bcfe*; and the Curie surface, *cdgf*. The lines of equi-hardness—the scleroscope hardness—of the ternary alloys are shown in Fig. 301. H. Kühlewein studied the mechanical and physical properties of

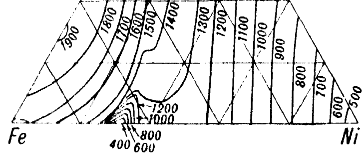


FIG. 304.—Intensity of Magnetization Curves of the Fe-Co-Ni Alloys.

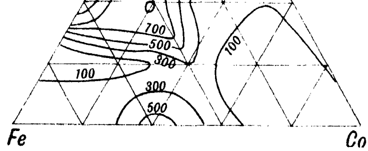


FIG. 305.—The Initial Permeability, μ_0, for the Annealed, Ternary Alloys.

these alloys. K. Honda found that the alloy 63·5 per cent. iron, 31·5 per cent. nickel, and 5 per cent. cobalt has a smaller coeff. of thermal expansion than that of fused silica.

G. W. Elmen studied the electrical resistance of the ternary alloys; the results are summarized in Fig. 302. H. Kühlewein summarized in Fig. 303 the observed results for the electrical resistance, $R \times 10^4$ ohm, of the ternary alloys. H. Masu-

moto found that the magnetization of the irreversible alloys, and of the H-solid soln. is difficult, but that of the reversible alloys is easy. The intensity of magnetization curves are summarized in Fig. 304. The small value for an iron-nickel alloy with 30 per cent. of nickel gradually increases with the addition of increasing proportions of cobalt, until finally, it attains its ordinary value, when 79 per cent. of cobalt and 21 per cent. of iron are present. G. W. Elmen, U. Meyer, and T. D. Yensen studied the magnetic properties of the ternary alloys. G. W. Elmen's results for the initial and maximum permeabilities of the alloys are summarized in Figs. 305, 306, and 307. G. W. Elmen applied the term *perminvar*

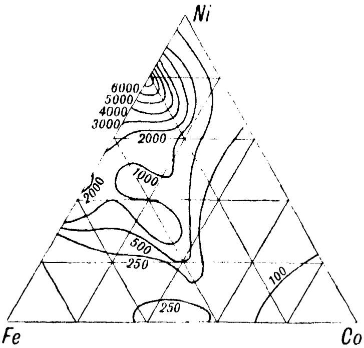


FIG. 306.—The Initial Permeability, μ_0, for the Air-Quenched, Ternary Alloys.

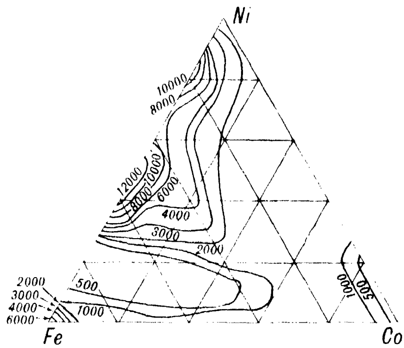


FIG. 307.—The Maximum Permeability for the Annealed, Ternary Alloys.

to those alloys—say Fe : Co : Ni=45 : 25 : 30—which gave a constant permeability for a long range in the magnetization curve, a small hysteresis loss in the same range, and a hysteresis loop constricted at the origin for medium flux densities. The initial magnetic permeabilities are summarized in Fig. 308, which shows that

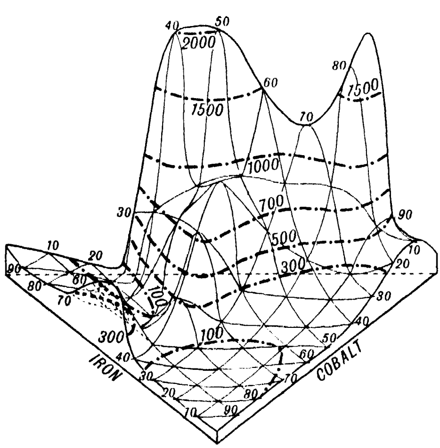


FIG. 308.—Initial Permeabilities of the Annealed Ternary Fe-Co-Ni-Alloys.

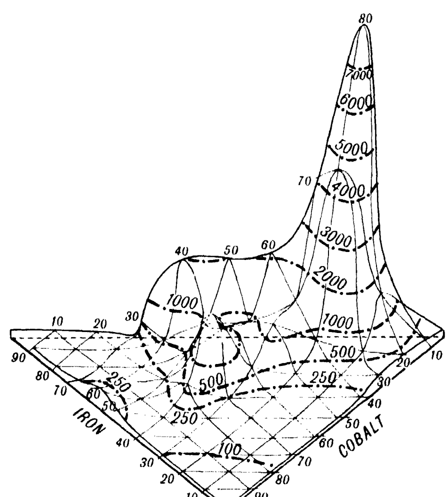


FIG. 309.—Initial Permeabilities of Air-Quenched, Ternary Fe-Co-Ni Alloys.

there are three regions of special interest—(i) the binary nickel-iron alloys; (ii) the ternary series in front of the first maximum in the iron-nickel series; and (iii) between 40 and 70 per cent. iron in the iron-cobalt series. Air quenching alters the results as indicated in Fig. 309. Observations were reported by

W. T. Griffiths, E. Gumlich and co-workers, F. Stäblein, H. D. Arnold and G. W. Elmen, H. Kühlewein, and U. Meyer. H. Masumoto's results for the induction, B gauss, refer to a field-strength $H=50$ gauss ; and those in Fig. 310, for a field strength $H=1400$ gauss. G. W. Elmen's values for the intrinsic magnetic inductions for annealed alloys respectively with different values of H

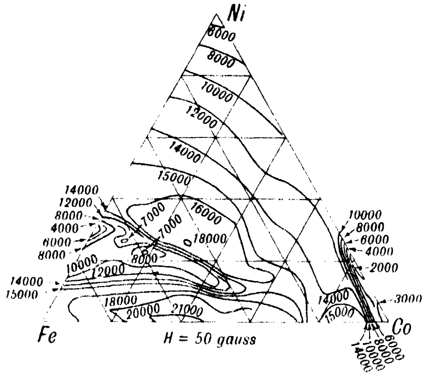


FIG. 310.—The Magnetic Induction, B, of the Ternary System.

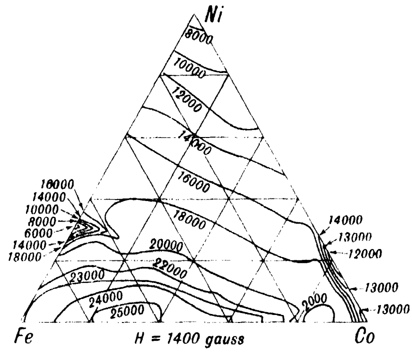
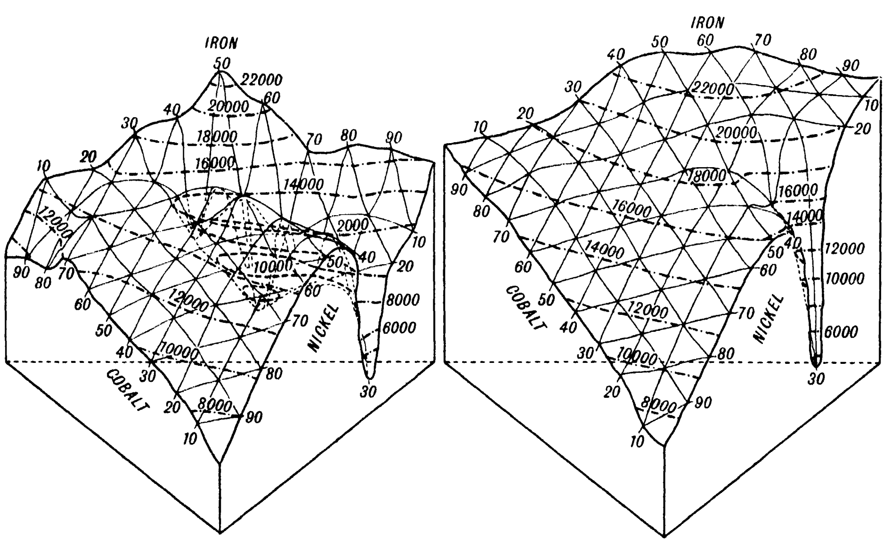


FIG. 311.—The Magnetic Induction of the Ternary System.

are shown in Figs. 312 and 313. G. W. Elmen's values for the hysteresis losses in ergs per sq. cm. per cycle are indicated in Fig. 314. Observations were made by O. E. Buckley and L. W. McKeehan, V. Retzow, W. T. Griffiths, J. F. Dillinger and R. M. Bozorth, J. F. Kayser, O. von Auwers and H. Kühlewein, K. Zschiesche, and E. Gumlich and co-workers. G. W. Elmen's values for the hysteresis losses in



FIGS. 312 and 313.—Intrinsic Inductions for Annealed Fe-Ni-Co Alloys.

ergs per cm. cube per cycle for a maximum flux density of 5000 gauss for the annealed alloys are summarized in Fig. 315.

The diagram for the iron-cobalt-nickel alloys, Fig. 299, has three zones where the crystalline structures are different : zone I has a body-centred cubic lattice—the α-form ; zone II, a face-centred cubic lattice—the γ-form ; and zone III, a close-packed hexagonal lattice—the H-form. The latter occupies but a relatively

small area. H. Kühlewein thus summarized the properties of alloys falling in the different zones :

The α-zone.—Here the alloys have the highest saturation capacity, for the induction B attains 25,000 gauss, whereas the value for iron alone is 22,000 to 23,000 gauss ; the binary alloy of iron with 30 per cent. cobalt has the highest value of all. When nickel is added to this alloy the maximum steadily decreases to $B=8000$ gauss, the value for nickel, without interfering much with the A_3-arrest, or the H-zone. The maximum is very flat, so that the possible existence of a cobalt diferride, Fe_2Co, is not excluded. However, neither the equilibrium diagram nor the specific properties of the cobalt-nickel alloys show any marked peculiarities in this region. The torsion modulus, however, has a maximum, and H. Masumoto and S. Nara observed a small maximum in the coeff. of thermal expansion, but A. Schulze could not confirm this. The 50 : 50 iron-cobalt alloy is very easily magnetized ; and the electrical and thermal conductivities of the binary alloys with 45 to 70 per cent. cobalt are higher than those of either constituent, a fact which has been attributed to the presence of an α-cobalt.

The γ-zone.—The binary alloys of iron with about 75 per cent. of nickel—permalloy—have very high permeabilities, and small hysteresis losses. Other specific properties of these binary alloys depend on the composition. The magnetostriction of iron is positive, that of nickel is negative, and there is a change of sign with about 81 per cent. of nickel,

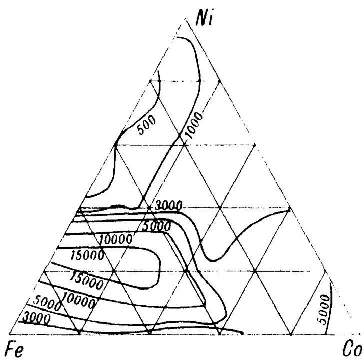


FIG. 314.—The Hysteresis Losses for the Ternary Alloys.

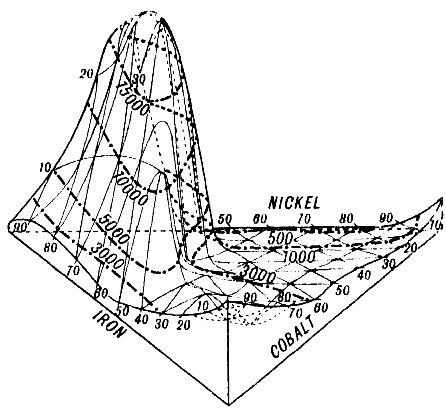


FIG. 315.—Hysteresis Losses for Annealed Co-Fe-Ni Alloys.

and the magnetostriction is zero. The torsion and elastic moduli have maxima with about 82 per cent. of nickel, and the specific heat has a minimum. In the vicinity of the A_3-transformation, with 30 per cent. of nickel, the torsion and elastic moduli have minima, and the sp. ht. has a maximum. The electric resistance attains a steep maximum, and the coeff. of thermal expansion a minimum nearby -36 per cent. of nickel gives the alloy invar. Some alloys are sensitive to heat treatment, and the perminvar exhibits a narrowing of the hysteresis loop. An explanation is based on the assumption that the alloy has two different components.

The αγ-zone.—These alloys are heterogeneous ; they contain two constituents whose proportions vary with temp. ; and accordingly also the specific properties. The properties of these alloys are thus very sensitive to heat treatment. These alloys are mechanically and magnetically hard. The A_3-transformation of the ternary alloys corresponds with a maximum in the electrical resistance, and probably also a minima in the torsion and elastic moduli.

The H-zone.—Alloys with about 95 per cent. of cobalt and 5 per cent. of nickel furnish alloys with a hexagonal lattice. The mechanical hardness attains a maximum, and also the magnetizability is a maximum in a very small field.

The γH-zone.—This zone is very small, and the properties of the corresponding alloys have not been closely investigated.

The emissivity of an alloy—*konel*—of nickel, cobalt, iron, and titanium was measured by E. F. Lowry. The effect of cobalt on high-speed tool-steels was discussed by K. Sasagawa, and L. Guillet.

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§ 10. Nickel Suboxides and Nickel Monoxide

A series of *nickel suboxides* has been reported, but there is some doubt whether any of them can be regarded as chemical individuals. There is a well-defined *nickel monoxide*, or *nickelous oxide*, NiO, commonly understood by the term "nickel oxide"; and a doubtful *nickelic oxide*, *nickel hemitrioxide*, or *nickel sesquioxide*, Ni_2O_3. Some intermediate oxides have been reported, *e.g.* *nickelosic oxide*, Ni_3O_4, as well as other doubtful intermediate oxides. There is also a *nickel dioxide* or *nickel peroxide*, NiO_2. Still higher oxides, *nickel tetraoxide*, NiO_4, and a *nickel hemipentoxide*, NiO_5, have been reported; and salts of the unknown *nickel trioxide*, NiO_3, have been described.

R. Tupputi [1] said that **nickel suboxide,** possibly, or **nickel hemioxide,** Ni_2O, was formed when nickel is heated in air; and W. Müller said that this oxide is formed as an intermediate product in the reduction of nickel oxide by hydrogen between 210° and 214°. I. L. Bell also said that this oxide is formed along with some carbon when nickel oxide is reduced by carbon monoxide free from cyanogen. The curves representing the speed of reduction of nickel oxide by hydrogen in the presence of a desiccating agent, obtained by E. Berger, and P. Sabatier and L. Espil, do not give unequivocal evidence of the existence of the hemioxide. T. Bedford and E. Erdmann assumed that nickel hemioxide is formed as an intermediate product in the hydrogenation of unsaturated organic compounds, but G. Bartels could not confirm the hypothesis. C. Kröger studied the thermal dissociation of the oxide.

According to P. D. Merica and R. G. Waltenberg, the 0·05 to 6·5 per cent. of oxygen contained in nickel is present in the form of NiO, and it forms a simple eutectic served with nickel stable at least up to 25 per cent. of nickel oxide, and probably up to the m.p. of nickel itself. The m.p. of nickel is 1552°, and of nickel oxide, NiO, 1656°. Nickel oxide dissolves in nickel, forming a eutectic with about 0·24 per cent. of oxygen corresponding with 1·1 per cent. of NiO. The eutectic mixture melts at 1438°, *i.e.*, about 14° below the m.p. of nickel. L. Wöhler and O. Balz were unable to confirm the existence of a nickel suboxide. G. R. Levi and G. Tacchini measured the relative intensities of the X-ray spectral lines of nickel, the suboxide, and the monoxide, and the results, Fig. 316, show that none of the reported methods of preparation furnish the suboxide. P. Sabatier and L. Espil reported that **nickel tetritaoxide,** Ni_4O, is formed when the suboxide is

reduced by hydrogen at 155° to 250°. T. Moore said that **nickel tritadioxide,** $Ni_3O_2.2H_2O$, is formed by boiling a soln. of potassium nickel cyanide with a reducing agent, adding ammonium chloride to the red soln., washing the product in succession with hot water, hot dil. aq. ammonia, and hot water, and drying it at 100°. It is said to react with silver nitrate in accord with the equation $Ni_3O+4AgNO_3=2Ni(NO_3)_2+NiO+4Ag$. I. Bellucci and R. M. Corelli saw that the reaction with silver nitrate is not sufficient to establish the composition of the tritadioxide, and they gave three analytical methods—(i) the evolution of hydrogen from a warm soln., (ii) the titration of the liquor with a 0·1*N*-soln. of iodine, and (iii) the titration of the liquor with standard hydrogen dioxide—which agree that the nickel contained in the liquor is univalent. This favours the view that the liquor contains a salt of the hemioxide, Ni_2O. C. Tubandt and W. Riedel, and L. A. Tschugaeff and V. G. Tschlopin assumed that the liquid obtained when a soln. of nickel cyanide is electrolyzed between platinum electrodes contains **nickel tritaoxide,** Ni_3O.

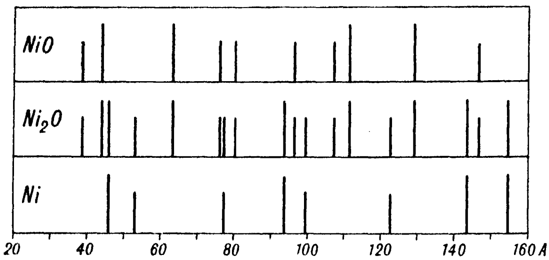

FIG. 316.—The Relative Intensities of the X-Ray Spectra of Nickel, the Suboxide and the Monoxide.

C. Bergemann [2] described green crystals of a mineral which occurs in cavities in the uranium, bismuth, and lead ores at Johanngevrgenstadt, Saxony, and J. D. Dana called the mineral **bunsenite**—after R. Bunsen. The deposit was described by A. Frenzel. Brownish-black, microscopic crystals of apparently the same oxide were reported by F. A. Genth to occur in some rosette copper from Riechelsdorf. The mineral was also described by F. Sandberger. Detailed analyses of the mineral have not been reported, but all the evidence indicates that bunsenite is **nickelous oxide,** or **nickel monoxide,** NiO. This oxide is readily obtained as a greenish powder, or in small, green crystals. J. A. Darbyshire found that thin fibres are transparent and almost colourless by transmitted light, and very pale pink by reflected light. Analyses of the oxide were reported by M. H. Klaproth, J. B. Richter, E. Rothoff, R. Tupputi, J. L. Proust, J. L. Lassaigne, O. L. Erdmann and R. F. Marchand, W. J. Russell, J. L. C. Zimmermann, L. Mond and C. Langer, I. L. Bell, and by some of the observers of the atomic weights of nickel. These all agree with the empirical formula $(NiO)_n$.

The preparation of nickel monoxide.—Nickel oxide is formed when nickel, nickel hydroxide, and the salts of nickel and a volatile acid are calcined or roasted in air. O. L. Erdmann observed that the oxide so obtained contains some nickelic oxide which can be removed by heating the oxide at 100° in hydrogen. E. R. Schneider obtained the monoxide by calcining the nitrate, and W. J. Russell added that if insufficiently heated the product contains some nickelic oxide. T. Andrews discussed the preparation of an oxide easily reduced to metal. The oxide obtained by roasting the nitrate, carbonate, or hydroxide in air was found by M. le Blanc and H. Sachse, and M. Prasad and M. G. Tendulkar to liberate iodine from an acidic soln. of potassium iodide; the proportion of active oxygen contained in the oxide decreases as the temp. of preparation is raised. J. L. C. Zimmermann said that if the oxide is heated in a current of nitrogen or carbon dioxide to a constant weight the product is free from the higher oxides. T. Vorster added that if reducing gases are present during the calcination, the product may contain some nickel—*vide supra,* nickel suboxides. W. N. Ipatéeff heated the metal, reduced in hydrogen at 270°, in air at the same temp., but found that incomplete oxidation occurs since the films of nickel oxide which are formed protect the underlying metal. Complete oxidation occurs at 400°. No higher

oxide of nickel is formed in dry or moist air, at ordinary or higher pressures, within the temp. interval 220° and 480°. The temp. of oxidation of reduced nickel is lowered by the presence of moisture. C. M. Loane obtained the oxide for use as a catalyst by the low temp. oxidation of the pyrophoric metal.

P. Sabatier and J. B. Senderens obtained nickel monoxide by heating nickel to at least 200° in a current of nitric oxide. O. L. Erdmann, and A. Laurent obtained nickel monoxide by calcining ammonium nickel nitrite; H. Baubigny, by calcining nickelosic oxide; F. Glaser, by heating nickelosic oxide in hydrogen at 198°; H. Moissan, and W. L. Dudley, hydrated nickelosic oxide; H. Moissan, W. Müller, and C. R. A. Wright and A. P. Luff, by calcining nickelosic or nickelic oxide in air or in hydrogen at 190° to 230°, or, according to T. Vorster, in a current of ammonia, or in a sealed tube at 150°; O. L. Erdmann, by roasting the chloride, or basic iodide; H. Schulze, by roasting the bromide; C. F. Rammelsberg, by roasting the iodate; A. Wächter, by roasting the chlorate; and C. Poulenc, by heating potassium nickel fluoride in air. C. Geitner prepared nickel oxide by heating nickel with a neutral soln. of sodium sulphate in a sealed tube at 200°. A. Coehn and M. Gläser obtained nickel oxide at the anode during the electrolysis of a soln. of a nickel salt and sodium acetate.

Crystals of nickel monoxide resembling bunsenite were prepared by J. J. Ebelmen by heating nickel borate with lime in a pottery oven, and washing away the soluble products with cold hydrochloric acid; by H. V. Regnault, and P. Sabatier and J. B. Senderens by heating nickel to dull redness in a current of steam, or by heating nickel with potassium nitrate; by H. Debray, and H. Grandeau, by heating a mixture of nickel phosphate and potassium sulphate; by C. Lepierre and M. Lachaud, by roasting nickel sulphate; by H. V. Regnault, by heating a mixture of nickel chloride and sodium carbonate, and washing away the soluble matter; by M. Ferrières and E. Dupont, by heating nickel chloride in a current of steam; by H. Grandeau, by heating a mixture of nickel phosphate and potassium sulphate in air, and washing away the soluble salts; by J. A. Hedvall, by repeatedly heating the powder in an excess of potassium chloride whereby minute octahedral crystals are formed; and by E. W. von Siemens and J. G. Halske, by heating the oxide in an electric furnace. V. Kohlschütter and J. L. Tüscher prepared an aerosol of the oxide; and H. P. Walmsley studied the sp. gr. of the particles of the aerosol.

The physical properties of nickel monoxides.—The **colour** of nickel oxide has been reported to be olive-green when prepared at a white heat (P. Berthier); greyish-greenish-yellow (O. L. Erdmann); greyish-black (R. Tupputi); and green (W. J. Russell, and H. Grandeau). T. Vorster said that the colour is yellowish-grey when cold, and when heated, yellow. J. L. C. Zimmermann also noted that the green powder becomes yellow when heated, and on cooling, the green colour is restored. G. Tammann and C. F. Marais discussed the colour of thin films of nickel oxide—*vide* nickel. H. Moissan said the crystals obtained by cooling the molten oxide are green. M. Centnerszwer and H. Zyskowicz obtained dark blue nickel oxide by the action of air, oxygen, or nitric oxide on nickel at 280° to 290°, and the colour is retained at 290°, but above this temp., the colour becomes yellowish-green. C. Bergemann said that the mineral bunsenite is pistachio-green, and the powder or streak is brownish-black. M. le Blanc and H. Sachse obtained the oxide in colours ranging from dark grey to greyish-green, by heating the basic carbonate to temperatures between 550° and 1220°. M. Prasad and M. G. Tendulkar observed that the products obtained by heating the nitrate in air have these characteristics:

Temperature .	400°	500°	800°	900°	1000°
Nickel oxide .	99·15	99·61	99·91	100	100 per cent.
Colour . .	Black	Grey	Grey-green	Greenish-yellow	

Analogous results were obtained with the basic carbonate. The basic carbonate and hydroxide, in vacuo at 400° to 500°, furnish a greenish-yellow oxide which

becomes black on exposure to air, but not so with the greenish-yellow oxide prepared by heating the basic carbonate to 800°. The original colour is restored if the blackened oxide be heated in vacuo at 200°. The blackened product is thought to be an adsorption product of the oxygen from the air since M. le Blanc and H. Sachse observed that the X-radiogram of the blackened oxide corresponds with nickel monoxide with surplus oxygen interstitially associated with the lattice —*die vagabunierenden Atomen*—*vide* Fig. 330, **13.** 66, 17. The blackened product also liberates iodine from a soln. of potassium iodide. G. Bruni and A. Ferrari studied the solid soln. of the oxides.

The transparent, octahedral, greenish **crystals** belong to the cubic system. The octahedra of bunsenite sometimes have truncated edges. F. M. Bravo found that the **X-radiograms** correspond with a cubic, face-centred lattice of the sodium chloride type, and having the side $a=4{\cdot}244$ A.—*vide* Fig. 316 for the X-ray spectrum. There are 4 mols. per unit cell. G. Natta, S. B. Hendricks and co-workers, V. M. Goldschmidt and co-workers, and G. Lunde gave $a=4{\cdot}17$ A.; G. D. Preston, 4·10 A.; O. G. Bennett and co-workers, 4·1684 A.; G. L. Clark and co-workers, 4·16 A.; S. Holgersson and A. Karlsson, 4·181 A.; G. R. Levi and G. Tacchini, 4·18 A.; W. P. Davey, 4·14 A.; W. P. Davey and E. D. Hoffman, 4·20 A.; J. Brentano, 4·1705 A. to 4·1720 A.; and C. J. Ksanda, 4·171 A. O. G. Bennett and co-workers reported that the oxide prepared at a low temp. does not possess a face-centred cubic lattice, but is another cubic modification with $a=4{\cdot}64$ A., and 4 mols. per unit cell, and sp. gr. 4·8. W. L. Bragg and J. A. Darbyshire found that thin films have the same structure as the ordinary oxide. Observations were also made by J. A. Hedvall, and R. Smoluchowsky. O. Hahn and O. Müller studied the adsorption of radium emanation by nickel oxide.

C. Bergemann gave 6·398 for the **specific gravity** of bunsenite; J. J. Ebelmen gave 6·80; and F. A. Genth, 6·605, and for a furnace product, 5·745. For the artificial oxide, C. F. Rammelsberg gave 6·661; J. J. Ebelmen, 6·8; L. Playfair and J. P. Joule, 5·597; J. A. Hedvall, 7·45; H. Schröder, 6·60 to 6·80; and C. Lepierre and M. Lachaud added that the oxides obtained from the two modifications of the hydrated sulphate have, respectively, the sp. gr. 6·67 and 6·70—the higher value belonging to the octahedral form. F. M. Bravo calculated 6·827 from the lattice constants, and C. J. Ksanda, 6·8. H. P. Walmsley studied the sp. gr. of the particles of the aerosol. M. Prasad and M. G. Tendulkar found that the sp. gr. at 28°/4° varied with the temp. of preparation, thus,

	400°	500°	700°	800°	900°	1000°
Specific gravity .	5·668	5·745	6·070	6·265	6·305	6·310

The oxide undergoes a marked shrinkage when prepared at 800°. The greenish-yellow oxide settled in water more quickly than the grey form. The intramolecular change starts somewhere between 700° and 800°, and is completed at 1000°. W. Biltz studied the mol. vol. G. Bruni and A. Ferrari discussed solid soln. with nickel oxide. C. Bergemann, and others have given 5·5 to 6·0 for the **hardness** of bunsenite on Mohs' scale. A. Reis and L. Zimmermann studied the subject. H. V. Regnault found the **specific heat** of the feebly-calcined oxide to be 0·1623, and that of the strongly-calcined oxide, 0·1588—when the respective **atomic heats** were 12·1 and 11·9. L. Elsner observed the **volatility** of the oxide in a porcelain oven; and A. Baubigny observed no dissociation of the oxide at the highest temp. of a reverberatory iron furnace. G. Kröger, W. Stahl, J. Hagenacker, H. W. Foote and E. K. Smith, and N. Parravano and G. Malquori studied the **thermal dissociation** of the oxide—*vide infra.* A. Kapustinsky and L. Schamonsky found the partial press. p mm., of oxygen in nickel oxide to be:

	1147°	1177°	1237°	1257°	1337°
p	$2{\cdot}24\times10^{-6}$	$3{\cdot}41\times10^{-6}$	$1{\cdot}68\times10^{-5}$	$3{\cdot}21\times10^{-5}$	$1{\cdot}97\times10^{-4}$

or $\log K_p=\log p=23{,}250T^{-1}+10{,}678$.

H. Moissan said that the oxide melts in the electric arc furnace, and then solidifies to a mass of green crystals. P. D. Merica and R. G. Waltenberg gave 1652° for the **melting point** of the black oxide, and 1660° for that of a purified sample; H. von Wartenberg and H. J. Reusch gave 1990° for the m.p.; and H. Wartenberg and W. Gurr, 2090°. M. Berthelot discussed the **heat of formation** of the oxide; W. A. Roth gave 58·6 Cals.; P. L. Dulong, 59·7 Cals.; R. N. Pease and R. S. Cook, 54·15 Cals.; D. Müller, 58·64 Cals.; W. G. Mixter, 57·9 Cals.; A. Kapustinsky and L. Schamonsky, 53·15 Cals.; F. Giordiani and E. Mattias, 54·490 Cals.; O. Ruff and E. Gersten, 51·5 Cals.; M. Watanabe, 57·112 Cals. at 25°; W. A. Roth, 58·9 Cals.; and A. Skapsky and J. Dabrowsky, 54·898 Cals., and they also gave for the effect of temp., $Q=57,388+0·94T+0·00192T^2-0·0_674T^3$ cals. R. N. Pease and R. S. Cook gave for the **free energy** of nickel monoxide, $Ni+\frac{1}{2}O_2=NiO$, at $T°$ K., $F=-53,763+0·94T \log T+0·00165T^2-0·0_637T^3+10·64T$, or, at 25°, *i.e.*, 298° K., $-56,467$ cals. M. Watanabe gave $-57,739-5·44T \log T-0·000824T_2+38·05T$; or $-50,333$ cals. at 298°. The subject was studied by G. Beck, and R. von Dallwitz-Wegner. M. Watanabe gave 8·97 cals. per degree for the **entropy** of nickel oxide. G. Beck studied the subject.

A. Kundt gave for the **index of refraction,** 2·18 for red light; 2·23 for white light; and 2·39 for blue light; and C. J. Ksanda gave 2·37 for Li-light. F. Allison and E. J. Murphy studied the magneto-optical properties. According to G. K. Burgess and P. D. Foote, the **emissivity** of nickel oxide for monochromatic red light of wave-length $0·65\mu$, decreases as the temp. rises from 700° to 1300°; and it increases as the wave-length increases from $0·5\mu$ to $0·7\mu$. There is a broad absorption band in the ultra-red. Between 700° and 1200°, the total emission increases approximately as a linear function of the temp., but between 1200° and 1300° the rate of increase is smaller. A. Wehnelt said that the oxide is inactive in emission of electrons when fixed on a platinum disc and used as cathode of a discharge tube. M. Kahanowicz represented the emissivity, E, by $E=1·36\times10^{-10}T^4e^{-504·1/T}$.

H. G. Howell and G. D. Rochester studied the **absorption spectrum** of the nickel oxides. R. Smoluchowsky, J. Shearer, M. Ishino and K. Kojima, R. W. G. Wyckoff, and J. Veldkamp studied the **X-ray spectrum**; R. W. G. Wyckoff, the X-ray scattering power; A. Karl, the **triboluminescence** of the oxide; K. Fischbeck, and F. Jentzsch, the thermal **emission of electrons**; J. E. Nyrop, the surface electrons; J. A. Darbyshire, the **diffraction of electrons** by nickel oxide; and G. Tammann and G. Veszi, the action of cathode electrons on the colour of thin layers. R. Robl observed no luminescence in **ultra-violet light.**

F. Beijerinck said that the mineral bunsenite is a non-conductor of electricity. M. Prasad and M. G. Tendulkar found the **electrical resistance,** R ohms, to be, for the oxide prepared at

	400°	600°	700°	800°	900°
R	4·880	7·598	9·034	14·772	Very high

M. le Blanc and H. Sachse found the sp. conductivity of yellow nickel oxide, of a high degree of purity, prepared in vacuo at 300°, and of black nickel oxide, obtained by heating the yellow oxide in oxygen at 100 mm. press. at 250°, to be:

	−150°	−50°	20°	100°	150°	300°	400°	480°	600°
Black oxide .	10^{-9}	$0·0_577$	$0·0_378$	0·0053	0·010	0·054	0·087	—	0·140
Yellow oxide	—	—	$<10^{-8}$	$<10^{-8}$	$0·0_718$	$0·0_790$	$0·0_556$	$0·0_451$	—

The results show the favourable effect of adsorbed oxygen on the conductivity—an oxide equivalent to $NiO+0·050\ O$, at 18°, had a conductivity of 10^{-3} mho. C. Wagner, H. H. von Baumbach and C. Wagner, and M. le Blanc and H. Sachse, W. Meyer, and C. Wagner discussed the electronic theory of the electrical conductivity. J. Zedner measured the **electromotive force** of the cell $NiO : KOH_{soln.} : H_2$—*vide supra,* nickel accumulator; and R. Goldschmidt, that of the cell

$NiO : K_2CO_{3soln.} : Zn$. G. I. Finch and J. C. Stimson studied the **potential** of nickel oxide on nickel against oxygen; and S. Jahn, the potential of nickel oxide electrodes against ozone. H. H. von Baumbach and C. Wagner studied the thermoelectric force. C. F. Rammelsberg said that the oxide is non-magnetic. W. Klemm and co-workers observed that with a sample of nickel oxide, *A*, obtained from the carbonate at 400° to 450°; *B*, from the carbonate at 350° to 400°; and *C*, from the carbonate at 500°, with magnetic fields of 2040, 2960, and 3630 gauss, the effect of temp. on the **magnetic susceptibility** is that indicated in Fig. 317. The dotted line represents the results with nickel salts. S. S. Bhatnagar and G. S. Bal obtained 9.56×10^{-6} mass unit, and showed that high values may be obtained if the oxide is contaminated with metal. R. B. James studied the magnetic properties of the oxide.

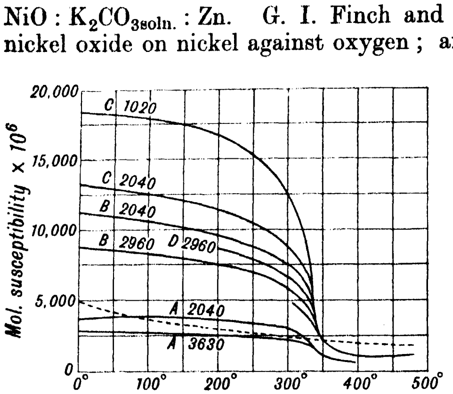

FIG. 317.—The Effect of Temperature on the Magnetic Susceptibility of Nickel Oxide.

The chemical properties of nickel oxide.—According to P. Schützenberger, when greenish-yellow nickel oxide, formed between dull redness and bright redness, is heated almost to a white-heat, it contracts considerably, acquires a deeper green tint, and loses 0·4 to 0·5 per cent. in weight. This loss takes place even in an atm. of nitrogen, and cannot be attributed to reduction, neither does it seem to be due to dissociation.

If the strongly-heated nickel oxide is reduced in hydrogen, the residue retains a small quantity of oxygen, but if allowed to remain at the ordinary temp. for 24 hrs. and again heated in hydrogen, a small quantity of water is immediately produced. Two or three repetitions of this process are required in order to remove the whole of the oxygen. J. A. Hedvall said that the oxide is stable at a red-heat. According to H. W. Foote and E. K. Smith, the **dissociation pressure** of oxygen, *p* mm., over nickel oxide at different temp. is:

	800°	900°	1000°	1100°	1200°	1245°
p	0·0	0·0	2·0	5·5	13·0	18·0

so that the dissociation of the oxide becomes appreciable as the temp. rises to 1000°. J. Hagenacker observed but a small dissociation press. at 1050°. G. Kröger studied the subject. W. Stahl calculated from the heat of formation, *Q*, smaller values than H. W. Foote and E. K. Smith for the dissociation press.; he gave $\log p = -Q/4{\cdot}57T + 1{\cdot}75 \log T + 2{\cdot}8$. M. Watanabe gave for the free energy of the dissociation $\delta F = -57{,}739 - 5{\cdot}44T \log T + 0{\cdot}000824T^2 + 30{\cdot}05T$; and for the dissociation press. $\delta F = -RT \log (1/p^{\frac{1}{2}}_{O_2})$; and

	25°	1000°	1100°	1200°	1227°	1245°
p .	$1{\cdot}2 \times 10^{11}$	$5{\cdot}9 \times 10^{-8}$	$1{\cdot}5 \times 10^{-6}$	$2{\cdot}4 \times 10^{-5}$	$4{\cdot}8 \times 10^{-5}$	$7{\cdot}5 \times 10^{-5}$

R. N. Pease and R. S. Cook gave for the equilibrium constant at 450°, 515°, and 570°, $p_{H_2O}/p_{H_2} = 67$, 57, and 50·5, respectively.

The early workers thought that nickel oxide passes into a suboxide when it is partially reduced by **hydrogen.** A. A. Read observed that nickel monoxide is reduced to metal when it is heated at the tip of a coal-gas flame, at, say, 1750°. In 1830, C. M. Despretz found that nickel oxide is reduced by hydrogen at the same temp. as that at which nickel is oxidized by water vapour, thus showing the reversibility of the reaction $H_2 + NiO = H_2O + Ni + 8{\cdot}8$ Cals. T. Vorster observed that nickel oxide is reduced by hydrogen more or less completely at 230°; F. Glaser said 230°; S. Hauser, 95° to 106°; W. Müller, and C. R. A. Wright and A. P. Luff, 220°; G. Gallo, 118° to 120°—*vide infra*, nickelic oxide. W. Ipatéeff found that at ordinary press., reduction begins at about 200°, but at higher press., the oxide

can be reduced at 172°. The temp. at which the oxide is reduced depends on the temp. at which the oxide has previously been heated. The reaction was studied by G. B. Taylor and H. W. Starkweather, A. F. Benton and P. H. Emmett, H. Saito, W. Biltz and H. Müller, E. Berger, and A. R. Ubbelohde. K. Grassmann and E. J. Kohlmeyer found that the V_2O_5, Cb_2O_5, Ta_2O_5, and CeO_2 are more readily reduced by hydrogen when they are mixed with nickel acids than they are when alone. G. Chaudron, and L. Wöhler and O. Balz made incomplete measurements of the equilibrium conditions in the reaction : $NiO+H_2=H_2O+Ni$, and gave 14·8 for the constant NiO : Ni, at 450°. R. N. Pease and R. S. Cook found that at 485°, the $H_2O : H_2$ ratio is 325, and at 600°, it is 240. They gave for the free energy, F, of the reaction $NiO+H_2=Ni+H_2O$, $F=-3647-6{\cdot}722T$. M. Watanabe gave for the free energy of the reaction $\delta F=329+7{\cdot}60T \log T +0{\cdot}000826T^2-0{\cdot}0_637T^3-34{\cdot}13T^{-1}$. A. Skapsky and J. Dabrowsky gave for the equilibrium constant $K=p_{H_2O}/p_{H_2}$,

	450°	500°	600°	650°	700°
K	21·6	17·3	13·4	11·7	9·8

P. H. Emmett said that the reaction is autocatalytic in that the metal produced in the course of the reaction acts as a catalytic agent on the subsequent course of the reduction. E. Berger, and G. Tammann and C. F. Marais studied the rate of reduction of nickel oxide by hydrogen ; and E. Berger said that nickel oxide is reduced more rapidly with dry hydrogen than it is with the moist gas. P. Sabatier and J. B. Senderens, J. B. Senderens and J. Aboulenc, P. Sabatier and L. Espil, W. Ipatéeff, F. Bedford and E. Erdmann, and W. Meigen and G. Bartels discussed the use of nickel oxide as a catalyst in hydrogenations—*vide supra*, the catalytic action of nickel.

T. W. Richards and E. F. Rogers found that nickel oxide prepared by the ignition of the nitrate readily occludes **oxygen** and other gases which are not given off when the oxide is dissolved in potash-lye. In one case, 4·11 c.c. of gas were obtained from 10 grms. of the oxide, and the gas contained 12·25 per cent. of oxygen, and 87·75 per cent. of nitrogen. M. Prasad and M. G. Tendulkar found that the oxide, prepared from the nitrate at temp. below 1000°, contained some nitrogen oxides, and when prepared from the basic carbonate, some carbon dioxide and water vapour. W. J. Russell observed that nickel monoxide, prepared at a high temp., does not take up oxygen from the air either at ordinary temp., or when it is heated. H. Dünwald and C. Wagner studied the diffusion of oxygen in nickel oxide. W. Ipatéeff found that nickel monoxide is not oxidized by dry or moist air ; or by oxygen at ordinary or at high press. within the temp. interval 220° to 480°, but H. Moissan observed that when obtained by calcination at 350° to 400°, oxygen is taken up from the air, and a black product is formed. The black oxide is decomposed and the absorbed oxygen is rejected when the temp. exceeds 600°. M. Prasad and M. G. Tendulkar found that the blackened oxide becomes greenish-yellow when heated in vacuo at 200°, or when placed in an acidic soln. of potassium iodide. The blackened oxide liberates chlorine from hydrochloric acid (W. J. Russell), and iodine from an acidic soln. of potassium iodide (M. le Blanc and H. Sachse). The greenish-yellow oxide obtained by heating the basic carbonate in vacuo over 800° does not absorb oxygen from the air. The blackened oxide is not nickelic oxide because that oxide does not behave similarly when heated in vacuo, or when placed in an acidic soln. of potassium iodide. M. Prasad and M. G. Tendulkar, and M. le Blanc and H. Sachse assumed that it is an adsorption complex of nickelous oxide with surplus oxygen associated interstitially with the lattice—*vide supra*. S. S. Bhatnagar and S. L. Bhatia studied the evaporation of adsorbed waters from the surface of nickel oxide. According to A. Mailfert, **ozone** readily oxidizes nickelous oxide to nickelic oxide.

J. J. Ebelman said that nickel oxide is insoluble in **water.** L. Passerini studied the solubility of the oxide. M. C. Boswell and C. H. Bayley discussed the catalytic

action of nickel oxide on hydrogen and oxygen, and the "poisoning" effect of chlorine. C. F. Schönbein observed that **hydrogen dioxide** attacks nickel monoxide with the brisk evolution of oxygen and the formation of a green higher oxide. A. Quartaroli showed that the decomposition of hydrogen dioxide by many metal oxides is autocatalytic, but J. Clarens said that the decomposition is a physical property dependent on the physical nature of the catalyst. The décomposition of a neutral soln. of hydrogen dioxide by nickel monoxide is slow, but it is faster with an alkaline soln. The velocity constants, k, for a unimolecular reaction, observed by M. Prasad and M. G. Tendulkar with nickel monoxide at 30° in an alkaline soln. of hydrogen dioxide, were:

	400°	500°	800°	1000°
$k\times10^4$ . .	81	46	16	8

S. Veil studied the reaction; and A. Quartaroli noted that the presence of nickel oxide diminished the activity of lead oxide as a catalyst.

H. Moissan observed that nickel monoxide becomes incandescent in **fluorine.** J. J. Ebelmen observed that the oxide prepared by calcination at a high temp. dissolves in acids much more slowly than does that produced at a low temp. R. Wasmuht studied the action of chlorine on the heated oxide. According to J. L. C. Zimmermann, the oxide obtained by calcining the hydroxide in carbon dioxide or nitrogen dissolves in hot, dil. or conc. **hydrochloric acid**—sp. gr. 1·124 to 1·185, yielding a green soln. without the formation of chlorine, and similarly with the conc. acid in the cold. Chloride is produced when traces of a higher oxide are present—*vide supra*. J. L. C. Zimmermann observed that nickel oxide forms a green soln. when warmed with **perchloric acid** of sp. gr. 1·155. G. H. Bailey and W. B. Hopkins show that the presence of this oxide favours the thermal decomposition of **potassium chlorate.**

R. Tupputi noted that when nickel oxide is heated with **sulphur,** nickel sulphide is formed, and J. A. Arfvedson, that a similar product is obtained when the oxide is heated in a current of **hydrogen sulphide.** J. L. C. Zimmermann found that nickel oxide dissolves slowly in warm **sulphuric acid** of sp. gr. 1·835, but it is very slowly attacked by the dil. acid of sp. gr. 1·135. The rate of dissolution of the oxide depends on the temp. at which it has been prepared. M. Prasad and M. G. Tendulkar found that when 0·2 grm. of oxide calcined at different temp. was treated with $0{\cdot}1N$-H_2SO_4 at 80°, under similar conditions, the following amounts of nickel oxide were dissolved:

	400°	500°	700°	800°	900°	1000°
NiO . .	96·86	85·70	36·70	2·68	2·18	0·77 per cent.

There is thus a marked difference in the behaviours of the black oxide prepared at 400°, and the yellowish-green oxide prepared at, say, 1000°—the former is active, the latter inactive. The activity may be due to a difference in the grain-size of the oxide, to the transition from an amorphous to a crystalline state, or to an intramolecular change. M. Prasad and M. G. Tendulkar also studied the action of sulphuric acid on mixtures of copper and nickel oxides prepared in various ways.

The solubility of **nitrogen** in nickel monoxide has been previously discussed. J. L. C. Zimmermann's observations, cited above, show that nitrogen has no chemical action on heated nickel oxide. G. Gore said that the oxide is insoluble in liquid **ammonia.** T. Vorster found that nickel oxide is reduced to the metal when heated above 200° in dry ammonia—H. N. Warren suggested the possibility of the formation of a nitride at higher temp. S. Hauser's results for the press. of nickel oxide in ammonia at a constant vol., temp. variable, and for the press. at a constant temp., 185°, with time variable, are summarized in Fig. 318. R. Tupputi found that nickel oxide dissolves slowly in aq. ammonia with the evolution of some nitrogen. The sat. soln. is azure-blue, when moderately concentrated it is

lavender-blue, and if dilute, violet-blue. When heated, the soln. gives off ammonia, and deposits crystals of nickel oxide. When exposed to air, nickel carbonate is precipitated, but not if a strong acid is also present. The fixed alkalies precipitate a complex of alkali and nickel oxide. J. Schlossberger found that the ammoniacal soln. dissolves silk, but not cellulose—*cf.* the ammoniacal soln. of cupric oxide. According to E. J. Houston, the soln. of nickel oxide in aq. ammonia is violet in colour, and it becomes pale blue when warmed. L. Santi found that the oxide is reduced to the metal when heated with dry **ammonium chloride,** but with an aq. soln. of that salt ammonia is evolved and nickelous chloride is formed. H. Moissan made observations to the same effect. J. L. C. Zimmermann observed that the oxide is insoluble in soln. of ammonium chloride; but H. Demarçay found that it dissolves slightly in a boiling soln. of that salt with the evolution of ammonia. J. L. C. Zimmermann observed that nickel oxide dissolves in warm **nitric acid,** of sp. gr. 1·32, forming a green soln.

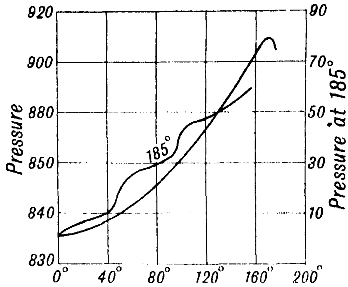

FIG. 318.—The Reduction of Nickel Oxide by Ammonia.

According to C. R. A. Wright and A. P. Luff, **carbon** begins to reduce nickel oxide at 450°. Observations on the subject were made by J. J. Berzelius, P. Berthier, O. L. Erdmann, G. Tammann and A. Y. Sworykin, W. Baukloh and R. Durrer, and R. Bunsen. B. Bogitch studied the reduction of nickel oxide by wood charcoal, and by coal. J. Garnier observed that molten nickel at a high temp. is very mobile and readily penetrates charcoal, forming, when cold, slender, hair-like filaments which are very flexible and malleable. H. Arnfelt studied the catalytic effect on the graphitization of coke. I. L. Bell said that cyanogen-free **carbon monoxide** reduces the monoxide to the suboxide—*vide supra.* M. Watanabe, F. Göbel, O. Boudouard, L. Belladen and A. Sommariva, and G. Charpy studied the reaction. C. J. Engelder and L. E. Miller found that the presence of titanic oxide promotes the activity of nickel oxide in the oxidation of carbon monoxide. T. Vorster, and C. R. A. Wright and A. P. Luff found that the reduction begins at about 120°. A. Laurent found that a mixture of equal parts of carbon monoxide and dioxide reduces nickel oxide without attacking the metal which is produced. According to O. Boudouard, the rate of reduction of nickel monoxide by carbon monoxide is faster than is the case with ferric oxide at 445°. The amount of decomposition increases with the quantity of oxide used and with the time. In all these cases, the amount of carbon deposited is of the same order of magnitude as that of the oxide employed; when a large excess of purified carbon is mixed with the oxide, the results obtained are, on the whole, the same as those already described, but the action takes place more slowly.

B. Bogitch, H. Saito, and G. Tammann and C. F. Marais studied the rate of reduction of nickel oxide by carbon monoxide. R. Schenck and H. Wesselkock studied the reduction of nickel oxide by carbon monoxide at 900°; and M. Watanabe between 663° and 852°. The equilibrium constant is independent of the composition of the solid phase, and the initial composition of the gas: $NiO+CO=Ni+CO_2$, and if the equilibrium constant $K_p=p_{CO_2}/p_{CO}$, $\log K_p=2590T^{-1}-0{\cdot}1082$. The thermal value of the reaction is $\delta Q=-9771-5{\cdot}11T+0{\cdot}003624T^2-0{\cdot}0_6062T^3$; and the free energy $\delta F=-9771+11{\cdot}77T\times\log T-0{\cdot}003624T^2+0{\cdot}0_631T^3-33{\cdot}59T^{-1}$. J. B. Richter thought that because nickel oxide is reduced to the metal in a porcelain oven, nickel should be included amongst the noble metals, but J. von Liebig and F. Wöhler, and A. Laurent showed that the observed effect is due to the action of carbon monoxide in the furnace, and not an effect of heat *per se.* J. L. C. Zimmermann's observations, cited above, show that **carbon dioxide** has no action on heated nickel oxide.

According to O. G. Bennett and co-workers, nickel oxide prepared at temp. not exceeding 110°, is a better absorbent of carbon dioxide at 56° than is the case with the oxide outgassed at 285°.

H. Hollings and R. H. Griffith studied the adsorption of **hydrocarbons** by nickel oxide. W. Ipatéeff found that in the presence of hydrogen and **benzene,** nickel monoxide is reduced at 172°, but with nickel oxide formed at a higher temp., catalytic reduction of the benzene occurs only above 200°; and the oxide itself is only slightly reduced—*vide supra,* nickel catalyst. When nickel oxide is heated in the vapour of **carbon tetrachloride,** H. Quantin observed that the oxide is converted into chloride. A. Kutzelnigg studied the action of the oxide on **potassium ferrocyanide,** and L. Hackspill and R. Grandadam, on **potassium cyanide.** J. L. C. Zimmermann found that the oxide is insoluble in a soln. of **ammonium thiocyanate**; and J. Milbauer, that molten **potassium thiocyanate** forms a complex $K_2Ni_{11}S_{10}$. J. Aloy and C. Rabaut noted that the presence of the oxide favours the hydrolysis of the **cyanohydrins.** W. L. Faith and D. B. Keyes studied the catalytic action of the oxide in the oxidation of **alcohol.** Nickel oxide as a catalyst for the dehydration of alcohol and **aniline** was studied by N. I. Shuikin. J. L. C. Zimmermann said that nickel monoxide is insoluble in **acetic acid** of sp. gr. 1·065. M. Centnerszwer and H. Zyskowicz found that the dark blue oxide is soluble in **organic acids,** but not in the ordinary organic solvents. H. Bodenbender observed that a litre of a soln. containing 418·6 grms. of **sugar** and 34·3 grms. of lime can dissolve 0·29 grm. of nickel oxide; A. Matagrin studied the action of organic substances on nickel.

C. H. Burgess and A. Holt observed that nickel oxide is not soluble in fused **boric oxide,** but if alkali or thallium oxides are present, nickel oxide is dissolved. W. Florence said that with fused **borax,** brown octahedral crystals are formed; and with **microcosmic salt,** apple-green, doubly refracting, hexagonal plates are formed. M. Rüger observed no combination of the oxide with **silica** at temp. between 900° and 1200°. H. von Wartenberg and co-workers represented the m.p. of mixtures of nickel oxide and **zirconia** by the curve, Fig. 68, **14.** 68, 10, in connection with cobalt oxide; the eutectic is at 2050°.

J. L. Gay Lussac and L. J. Thénard observed that **potassium** or **sodium** reduces nickel monoxide to the metal with a *lumière vive*; L. Franck, and B. Garre, that the reaction between **aluminium** and nickel begins at 600°, and evolves 106·5 Cals., and that between nickel oxide and **iron** begins at 640°, and evolves 7·8 Cals. The reaction was studied by L. B. Pfeil, and W. Jander and H. Senf. F. R. Hensel and J. A. Scott examined the solubility of nickel oxide in molten **nickel,** and G. Masing and L. Koch said that there is a eutectic at 1438° with 0·214 per cent. of oxygen.

E. Zinth and co-workers observed the formation of **sodium hyponickelite,** Na_2NiO, by the action of **sodium oxide** on nickelous oxide. J. L. C. Zimmermann observed that nickel monoxide is insoluble in a soln. of **potassium hydroxide.** A. Völker said that there is a slight solubility. G. Natta and L. Passerini calcined, over 600°, mixtures of calcium and nickel carbonates or hydroxides, and found that the X-radiograms of the products gave no evidence of a solid soln. between **calcium oxide** and nickel oxide. H. J. Reusch and H. von Wartenberg observed a eutectic at 1750° with nickel oxide and 36 per cent. of calcium oxide. J. A. Hedvall and co-workers studied the action of **barium peroxide.** L. Passerini, S. Holgersson and A. Karlsson, and H. von Wartenberg and E. Prophet observed that the corresponding mixtures of nickel oxide and **magnesium oxide** are miscible in all proportions, and that the displacement of the lattice is proportional to the composition. J. A. Hedvall and J. Heuberger studied the reaction with **magnesium sulphide.** G. Natta and L. Passerini observed that **zinc oxide** is partially miscible with nickel oxide, and that **cadmium oxide** is also miscible with nickel oxide. L. Passerini showed that displacement of the lattice is proportional to the composition. J. A. Hedvall and co-workers studied the

miscibility of nickel oxides with a number of other oxides when the mixture of oxides was heated to 900° with potassium chloride as a flux. With magnesium oxide, a homogeneous solid soln. is formed within the limits 27 to 90 per cent. NiO ; outside these limits, the crystals of the solid soln. are difficult to distinguish from those of the lone oxides. The cubic crystals are intermediate in colour between the colours of the compound oxides. With zinc oxide, hexagonal crystals of the solid soln. are formed when the zinc is in excess. Possibly a *nickel zincate* is formed which is miscible in an excess of zinc oxide. The colours of the crystals of the solid soln. are not strictly proportional to the colours of the compound oxides. E. Montignie studied the action of **mercuric chloride** on the oxide. J. A. Hedvall observed that nickel oxide forms blue octahedra or octahedral cubes of **nickel aluminate,** $NiO.Al_2O_3$, when it is heated with **alumina** ; an excess of either component can be readily detected microscopically. H. von Wartenberg and H. J. Reusch studied the m.p. of mixtures of alumina and nickel oxide ; W. Biltz and co-workers, the mol. vol. ; and S. Izawa, the luminescence of the mixtures. J. A. Hedvall found that nickel oxide reacts slowly with **stannic oxide,** below 1000°, forming a small proportion of **nickel stannate,** Ni_2SnO_4. F. de Carli noted that **lead dioxide,** at 250° to 300°, oxidizes nickel oxide to a higher oxide. W. E. Guerther, S. Holgersson and A. Karlsson, and S. Veil studied the reaction with **chromic oxide,** and the formation of nickel chromite, $Ni(CrO_2)_2$; and J. A. Hedvall found that solid soln. are formed with nickel oxide and **manganese oxide** ranging from NiO : MnO=1 : 5 to 5 : 1. The octahedra or octahedral cubes are yellowish-green. G. Natta and L. Passerini, L. Passerini, and S. Holgersson and A. Karlsson said that manganese and nickel oxides are miscible in all proportions, and that the displacement of the lattice is proportional to the composition. S. Roginsky and E. Shultz found the oxide to be an active catalyst in the thermal decomposition of **potassium permanganate.** R. F. Korte, N. Kawai, and S. Veil studied the reaction with **ferric oxide.** S. Veil studied the magnetic properties of nickel ferrite. L. Passerini, G. Natta and L. Passerini, and S. Holgersson and A. Karlsson found that **cobalt oxide** and nickel oxide are miscible in all proportions, and that the displacement of the lattice is proportional to the composition. J. A. Hedvall obtained octahedral crystals of the solid soln. ; and S. Veil studied the magnetization of the solid soln.

V. Tafel and F. Klewata studied the reaction with **cuprous sulphide ;** $2NiO+Cu_2S=2Cu+2Ni+SO_2-65{\cdot}4$ Cals. ; and E. Donath, and G. P. Schweder, the reaction with **ferrous sulphide,** $NiO+FeS=NiS+FeO$. According to J. L. C. Zimmermann, when nickel oxide is treated with fused **potassium hydrosulphate,** there is produced a dark brown substance which becomes yellow on cooling and forms a green soln. with water. C. Montemartini and A. Vernazza studied the action of nickel oxide on soln. of **chromic sulphate.**

The preparation of nickelous hydroxide.—Hydrated nickelous oxide, or **nickelous hydroxide,** $Ni(OH)_2$, or simply *nickel hydroxide*, was prepared by R. Tupputi [3] by treating a soln. of a nickel salt with alkali lye, or by heating an insoluble nickel salt with alkali lye, and dissolving out the alkali with boiling water. T. A. Edison made it for the nickel accumulator, by a somewhat similar process. L. Teichmann added that traces of the parent salt are retained by the hydroxide with great tenacity, and only from the nitrate did he succeed in preparing a product free from acid. He recommended washing the product first with cold water until the washings no longer show an alkaline reaction, then washing with ammoniacal water, and finally with hot water. According to J. Roszkowsky, the monobasic and polybasic organic acids prevent the formation of the hydroxides only in acidic or neutral solutions ; in alkaline solutions, a precipitate is nearly always obtained, although it is often some time in forming. Most of the organic compounds which prevent the formation of the hydroxides belong to the fatty series, and the corresponding aromatic compounds, with a few exceptions, are without influence. These, also, all contain the hydroxyl group, and if this group

is replaced by another monovalent basic or acid group, the compounds are formed without influence on the formation of hydroxide, except in the case of the amido-compounds, which form soluble complex salts. The hydroxide is produced when a soln. of nickel oxide or hydroxide in aq. ammonia is heated with potash lye (H. Rose); when nickel amminochloride is treated with alkali lye (H. A. Frasch), or boiled with water (O. L. Erdmann); when nickel tetramminonitrate or tetrammino-sulphate is boiled with water (A. Laurent, and O. L. Erdmann); or when a soln. of nickel carbonate in an excess of aq. ammonia is boiled (J. Pelouze and E. Frémy). O. L. Erdmann obtained the hydroxide by treating the basic iodide with boiling alcohol, or boiling alkali lye; S. E. Moody, by treating a soln. of nickel sulphate with a mixture of potassium iodide and iodate; F. Glaser, by the action of hydrogen on hydrated nickelic oxide; W. N. Ipatéeff, by exposing $0{\cdot}2N$-$Ni(NO_3)_2$, or a soln. of nickel acetate at 120°, to hydrogen under a press. of 100 atm.; and R. Lorenz, by using a nickel anode and a platinum cathode in a soln. of an alkali salt. C. A. Peters found that crystals of the hydroxide are slowly formed when a soln. of sodium chloride is allowed to stand over mercury with a nickel wire connecting both liquids. J. Zedner observed that in the discharge of a nickel accumulator (*q.v.*), the nickelic oxide passes into nickelous hydroxide. M. Roloff and H. Wehrlin prepared a mixture of nickelous and silver hydroxides by the action of alkali lye on a mixture of salts of the two metals. R. Saxon observed that the hydroxide is formed in the electrolysis of water with a nickel oxide.

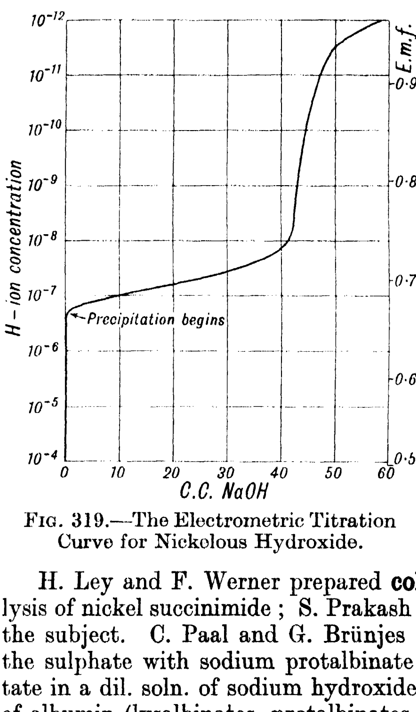

FIG. 319.—The Electrometric Titration Curve for Nickelous Hydroxide.

H. T. S. Britton, and H. T. S. Britton and R. A. Robinson titrated electrometrically, at 18°, 100 c.c. of a $0{\cdot}025M$-soln. of nickelous chloride with $0{\cdot}0967N$-NaOH, and the results are summarized in Fig. 319. The precipitation of the hydroxide began when the e.m.f. was 0·666 volt. corresponding with the value $p_H = 6{\cdot}66$, and when 0·6 c.c. of the soln. of sodium hydroxide had been added —51·7 c.c. of the soln. were theoretically required for complete precipitation.

H. Ley and F. Werner prepared **colloidal nickelous hydroxide** by the hydrolysis of nickel succinimide; S. Prakash and N. R. Dhar, and H. N. Holmes studied the subject. C. Paal and G. Brünjes obtained the colloid by treating a soln. of the sulphate with sodium protalbinate or lysalbinate, and dissolving the precipitate in a dil. soln. of sodium hydroxide; Kalle and Co. used the fission products of albumin (lysalbinates, protalbinates, alkali albumoses, etc.); A. V. Dumansky and B. G. Zaprometoff, mannitol and sodium tartrate; and L. Hugouneng and J. Loiseleur, glycogen as protective colloids. O. F. Tower and M. C. Cooke prepared colloidal soln. by two methods: one, by dialysing a solution of nickel tartrate in the presence of an alkaline solution of potassium tartrate; and the other, by treating a $0{\cdot}1N$-soln. of nickel chloride with a little more than the equivalent quantity of a solution of potassium hydroxide, allowing the precipitated nickel hydroxide to settle, siphoning off the supernatant liquid, adding water, and repeating the process several times. O. F. Tower also obtained the colloidal gel by the action of an alcoholic soln. of N-KOH on a soln. of nickel acetate in glycerol. The nickel hydroxide is said to be peptized by the presence of traces of potassium chloride. H. Knoche studied the peptization of the hydroxide by alkali hydroxides in the presence of chromic hydroxide; N. R. Dhar and S. Ghosh,

K. C. Sen and N. R. Dhar, and N. G. Chatterji and N. R. Dhar, by sucrose, dextrose, lævulose, galactose, lactose, mannose, dextrin, starch, and glycerol. K. C. Sen and N. R. Dhar obtained the colloidal soln. by dissolving the oxide in ammonia. The gel was prepared by H. N. Holmes. A. Lottermoser and F. Langenscheidt studied the freezing of the gels ; A. and E. Lottermoser studied the ageing of the hydrated oxide ; N. R. Dhar and A. C. Chatterji, the formation of rhythmic rings ; H. Tominga, the rate of sedimentation ; K. C. Sen, the adsorption of salts, etc. V. Kohlschütter and J. L. Tüscher prepared an **aerosol** of nickel oxide by oxidizing the vapour of the metal from an electric arc.

The properties of nickel hydroxide.—The nickelous hydroxide, analyzed by J. L. Proust, corresponded with the *tetritahydrate*, $4Ni(OH)_2.H_2O$, and similarly with the product, dried at 100°, analyzed by L. Schaffner. R. Tupputi said that the hydrated oxide usually appears as apple-green voluminous flakes. C. W. Stillwell said that nickelous hydroxide is laminar and amorphous, and if it is associated with cobaltous hydroxide, it makes the latter more stable. H. Arnfelt studied the passage from the amorphous state—X-radiograms first show diffuse bands which gradually sharpen into lines. The X-radiograms of the crystals were found by G. Natta to correspond with a rhombohedral lattice having a=3·07 A., and c=4·61 A., or $a : c$=1 : 1·50. R. W. Cairns and E. Ott gave a=3·114 A., and c=4·167 A. The sp. gr. calculated by G. Natta is 3·60. V. M. Goldschmidt and co-workers studied the subject. G. Natta and A. Reina found that the X-ray spectral lines of simultaneously - precipitated nickel and cobalt hydroxides showed that the two hydroxides are isomorphous. R. Smoluchowsky studied the X-ray absorption edges.

J. L. Proust found that nickel hydroxide gives off water when heated, but not so readily when the hydroxide has been boiled with water. A. Peter, and G. F. Hüttig and A. Peter found that with samples of hydrated nickelous oxide, prepared in different ways, A and B, Fig. 320, the dehydration temp. at 10 mm. press. is 230°, but to remove the last traces of water at that press. requires a temp. of about 360° ; thus water probably enters the lattice of nickelous oxide interstitially. The reaction $NiO.H_2O_{cryst.}=NiO_{cryst.}+H_2O$ is irreversible, so that if the monohydrate has a temp. range of existence, it is very small.

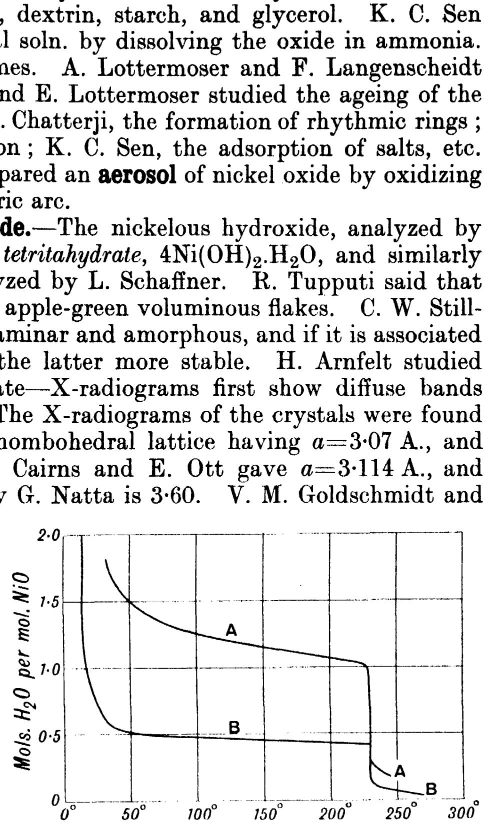

FIG. 320.—Dehydration Curves of Hydrated Nickelous Oxides.

O. F. Tower exposed samples of nickelous hydroxide, prepared from hot and cold soln. in atm. with a definite humidity until equilibrium was established, at 20°, and found, after 2 to 3 weeks' exposure, the following weights :

Press. aq. vapour		Original	3·79	3·73	2·24	0·85	0·15	0·00 mm.
Weight	Hot .	2·392	2·3808	2·3221	2·2516	2·1895	2·1858	2·1845 grms.
	Cold .	2·3024	2·2972	2·2465	2·1843	2·1251	2·1217	2·1209 ,,

The two samples behaved similarly except that the sample obtained from a cold soln. was rather more hygroscopic than that derived from a hot soln. The composition of both samples in the dried state corresponded closely with $Ni(OH)_2$, and not to NiO or to any intermediate hydrate of nickelous oxide. According to J. Thomsen, the heat of formation of nickel oxide is (Ni,O,H_2O)=60·84 Cals. ; F. Giordani and E. Mattias, 62·68 Cals., and for the heat of hydration, 8·19 Cals. ; J. Thomsen gave for the heat of neutralization $\{Ni(OH)_2,2HCl\,aq.\}$, 22·58 Cals., and with $SO_3aq.$, 26·11 Cals. M. Berthelot gave 11·265 Cals. for the heat of neutralization of $\frac{1}{2}Ni(OH)_2$ with nitric acid, and 13·055 Cals. with $\frac{1}{2}H_2SO_4aq.$

F. Giordani and E. Mattias gave 20·652 Cals. for 2·63N-HCl with $Ni(OH)_2$ at 20°, and with 5·52N-H_2SO_4, 22·165 Cals. at 28°. E. Petersen gave 13·835 Cals. for the heat of neutralization of $\frac{1}{2}Ni(OH)_2$ with hydrofluoric acid; and O. Mulert, 28·01 Cals. According to J. Thomsen, the heat of oxidation $\{2Ni(OH)_2,O,H_2O\}$ is $-1·3$ Cals.; and the heat of the reaction with hydrogen sulphide $\{Ni(OH)_2,H_2S\ aq.\}$ is 18·630 Cals. W. D. Treadwell calculated the heat of formation $(Ni,\frac{1}{2}O_2)$ $=61$ Cals. from the e.m.f., 0·855 volt, of the cell Ni,NiO (electrolyte of fused borax or glass) O_2, Ag at 800° to 1193°.

R. Robl observed no luminescence in ultra-violet light. H. T. S. Britton gave for the solubility product $[Ni^{\cdot\cdot}][OH']^2=8·7\times10^{-19}$. S. Labendzinsky, and R. Abegg and S. Labendzinsky found the e.m.f. of cells with solid nickelous hydroxide in a soln. of nickel nitrate against a calomel electrode to be 0·182 to 0·266 volt. S. Veil observed that the mol. coeff. of magnetization rises when the precipitated hydroxide is repeatedly dissolved and re-precipitated until it attains a maximum value, and that value is again increased when the hydroxide is immersed in hydrogen dioxide.

R. Tupputi found that nickel hydroxide is almost without taste, and that it is slightly soluble in water. R. W. Cairns and E. Ott observed no evidence of the formation of hydrates of $Ni(OH)_2$. G. Almkvist found that ordinary distilled water dissolves 12·7 mgrms. per litre at 20°. According to W. P. Jorissen and C. van den Pol, and N. N. Mittra and N. R. Dhar, in induced reactions involving the oxidation in air of nickelous, ferrous, cobaltous, cerous, and manganous hydroxides as secondary reactions, that of sodium sulphite is the primary reaction. A. Mailfert found that the hydroxide is easily transformed by ozone into nickelic oxide. T. Bayley said that the hydroxide is not changed by hydrogen dioxide, but C. F. Schonbein observed that there is slowly formed a paler coloured oxide which no longer decomposes the hydrogen dioxide, but it liberates iodine from a soln. of potassium iodide, and is possibly identical with the product obtained by the action of nickel monoxide on hydrogen dioxide. Nickel hydroxide is not oxidized in alkaline soln. by hydrogen dioxide, nor is it oxidized by sodium dioxide. A. Quartaroli, and S. Veil studied the decomposition of hydrogen dioxide by nickel hydroxide.

H. von Helmolt observed that with hot, neutral soln. of ammonium fluoride, a complex salt, $(NH_4)_2NiF_4.2H_2O$, is formed. O. Ruff and W. Menzel found that fluorine monoxide slowly oxidizes nickel hydroxide suspended in water, to form a peroxide. The reaction was studied by F. Forster, and F. Haber and F. Bran. Nickel oxide is oxidized in alkaline soln. by chlorine or bromine, but not by iodine; it is also oxidized by sodium hypochlorite, or bleaching powder, and the reactions were studied by A. J. Balard, R. Böttger, A. Carnot, H. Demarçay, R. Fischer, J. L. Lassaigne, J. L. Proust, R. W. Cairns and E. Ott, M. le Blanc and E. Möbius, and G. Schröder. E. Hayek studied the solubility of the hydroxide in soln. of its own salts.

The hydroxide dissolves readily in acids forming nickelous salts. C. Wicke reported that the hydroxide which has a slightly alkaline reaction becomes brown and then black on exposure to air containing sulphide owing to the formation of nickelic oxide, which is subsequently reduced to nickelous oxide by an excess of sulphur dioxide. F. Haber and F. Bran, and W. Reinders and S. I. Vles studied the oxidation of sodium sulphite in the presence of nickel hydroxide.

G. Gore observed that nickel hydroxide is insoluble in liquid ammonia. R. Tupputi found the hydroxide rapidly dissolves in aq. ammonia, forming a soln. which, as indicated above, was found by J. Schlossberger, to dissolve silk but not cotton. W. Bonsdorff found that at 25° the solubility of the oxide is:

NH_3	0·602N-	2·101N-	3·9N-	4·911N-
Ni (grm. per litre) . .	0·158	0·835	1·780	2·580
$Ni(OH)_2$ (equivalents) .	0·0054	0·0284	0·0607	0·0879

G. Stark obtained with N- and $2N$-NH_4OH, the respective concentrations $0{\cdot}014N$-Ni, and $0{\cdot}036N$-Ni. According to W. Bonsdorff, the solubilities here indicated are probably too low. D. P. Konowaloff, and H. M. Dawson and J. McCrae found that in ammoniacal soln. of nickel salts, probably $4NH_3$, are associated with each atom of nickel. W. Bonsdorff's data agree with the assumption that a complex $[Ni(NH_3)_4(OH)]_n$ is formed. W. Bonsdorff gave for the electrical conductivity, $K \times 10^4$, of ammoniacal soln. of nickel hydroxide :

NH_3	$0{\cdot}545N$-	N-	$3N$-	$5N$-	$7N$-	$10N$-
$Ni(OH)_2$ None . .	7·0	8·9	10·9	10·1	8·1	1·4
$Ni(OH)_2$ 0·0505 eq. .	12·7	14·7	16·0	14·7	12·6	9·6
$Ni(OH)_2$ 0·0101 eq. .	—	22·7	23·0	20·8	—	—

W. Bonsdorff obtained irregular results in attempting to obtain the e.m.f. of concentration cells containing nickel hydroxide dissolved in aq. ammonia. S. Veil studied the magnetic properties of the soln. F. and E. Rogers found that while nickelous hydroxide dissolves slowly in aq. ammonia, or in a soln. of ammonium carbonate, it readily dissolves when ammonium salts are present ; the hydroxide is also soluble in soln. of ammonium salts—*e.g.*, in boiling soln. of ammonium chloride. C. Reichard studied the adsorption of arsenious acid by the hydroxide. C. A. Wurtz found that the hydroxide is insoluble in methylamine, and in amylamine ; W. Traube and B. Löwe, that it forms with ethylenediamine a complex salt, $Ni(OH)_2.3C_2H_8N_2.8H_2O$; J. C. Duff and E. J. Bills, a complex salt, $3Ni(OH)_2.N(CH_2OH)_4$, with hexamethylenetetramine ; and G. T. Morgan and F. H. Burstal, probably a complex $[Ni(C_{10}H_8N_2)_3](OH)_2$, with tris-$\alpha\alpha'$-dipyridyl. O. F. Wiede and K. Hofmann obtained red crystals of nickel amminothiocarbonate, $Ni(NH_3)_3CS_3$, by the action of a mixture of ammonia and carbon disulphide on the heated hydroxide. F. and E. Rogers observed that nickel hydroxide dissolves in a soln. of potassium cyanide. P. N. Raikow studied the action of carbon dioxide hydroxide. O. F. Tower and M. C. Cooke observed that glycerol does not prevent the precipitation of nickel hydroxide from aq. soln., but J. Spiller found that the hydroxide is not precipitated in the presence of sodium citrate ; and H. Rose, that it is not precipitated in the presence of a number of non-volatile organic substances—*e.g.*, tartaric acid—*vide supra*, colloidal nickel hydroxide. P. Singh discussed the use of nickel hydroxide in the estimation of tannin. The action of silica on nickel oxide was studied by J. A. Hedvall and G. Schiller.

F. and E. Rogers, and A. B. de Schulten found nickel hydroxide to be insoluble in conc. soln. of potassium or sodium hydroxide. L. S. Lévy, M. Geloso and L. S. Lévy, and E. Toporescu observed that when ferric hydroxide is precipitated in the presence of nickel salts, some nickel hydroxide is adsorbed, and R. F. Korte noted that over 14 per cent. of nickel can be so adsorbed to form a solid soln. G. Natta and L. Passerini observed that nickel hydroxide forms a complete series of solid soln. with magnesium and cobalt hydroxides ; a partial series with zinc hydroxide, and no solid soln. with calcium hydroxide.

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§ 11. Nickelosic and Nickelic Oxides

H. Rose [1] described an oxide with rather more oxygen than corresponded with nickelous oxide, namely, $Ni_8O_9.H_2O$, or $6NiO.N_2O_3$. It was obtained as a black powder by calcining the basic carbonate at 300°; the water can be driven off without loss of oxygen. There are also some ill-defined oxides reported by C. F. Schönbein to be formed by the action of hydrogen dioxide on nickelous oxide or hydroxide.

H. Baubigny reported **nickelosic oxide,** or *nickel tritatetroxide*, Ni_3O_4, to be formed by heating nickelous chloride in a current of oxygen at 350° to 400°. The chloride turns black, and chlorine is given off. The reaction proceeds more rapidly in moist oxygen, and hydrogen chloride is then formed. W. L. Dudley obtained it by heating the dihydrate to 240°; and G. Schröder, by heating the trihydrate of nickelic oxide with potash-lye. F. Glaser said that nickelosic oxide is formed when nickel hydroxide is reduced by hydrogen at 188°, but W. N. Ipatćeff said that the product is really a mixture of nickel and of nickelous and nickelic oxides. W. L. Dudley obtained the *dihydrate*, $Ni_3O_4.2H_2O$, by melting sodium dioxide in a nickel crucible at a red-heat, and extracting the product in Sohxlet's apparatus with water; I. Bellucci and S. Rubegni worked similarly, but introduced some nickel oxide reduced by hydrogen in the molten sodium dioxide. The alkali is retained very tenaciously by the oxide. It was assumed that the alkali forms a nickelite, $Na_2Ni_3O_6$, which is hydrolyzed by water. F. Mawrow obtained the *hexahydrate*, $Ni_2O_3.6H_2O$, by heating nickelous oxide suspended in water with potassium persulphate; and, after boiling for 45 minutes, washing the product free from sulphates. The hexahydrate was then dried over sulphuric acid and calcium chloride, when it appeared as a greyish-black powder.

According to H. Baubigny, H. Moissan, and W. L. Dudley, anhydrous nickelosic oxide furnishes a grey or black powder consisting of microscopic, octahedral crystals which have the form of spinel. The dihydrate forms plates resembling graphite, which probably belong to the hexagonal system. The sp. gr. of the hydrate is 3·4115 at 32°. L. Wöhler and O. Balz observed that nickelosic oxide is less

stable than cobaltosic oxide, for it begins to decompose below 450°. The dihydrate is stable at temp. up to 130°, but at 140° it begins to lose weight, and at 240°, the weight remains constant and the product is Ni_3O_4; at a red-heat, there is a further loss in weight, and nickelous oxide is produced. F. Glaser said that nickelous oxide is formed at 198°. The oxide is not magnetic. M. le Blanc and E. Möbius obtained no evidence from the X-radiograms of the existence of hydrates of nickelosic oxide. R. W. Cairns and E. Ott studied the subject. W. Klemm and K. Hass investigated the magnetic properties.

E. Dufau, and I. Bellucci and E. Clavari denied the existence of nickelosic oxide, and supposed it to be a mixture of $NiO_2.2NiO$, and I. Bellucci and S. Rubegni prepared this oxide as just indicated—*vide infra.* D. K. Goralevitsch also gave some evidence in favour of the hypothesis that nickelosic oxide is a true chemical individual. G. L. Clark and co-workers attempted to determine the structure from the X-radiograms, but they found that the oxide is amorphous. The anhydrous oxide is hygroscopic, and at 30° it absorbs 7·4 per cent. of water from the atmosphere, and it loses this water at 110°. The oxide is soluble in acids. With hydrochloric acid, it gives off chlorine, and with sulphuric and nitric acids, it gives off oxygen. B. Newmann and co-workers studied the catalytic action on the oxidation of carbon monoxide.

The preparation of nickelic oxide and its hydrates.—There are numerous references in the literature to **nickelic oxide,** or *nickel hemitrioxide*, Ni_2O_3, but in some cases the term means an oxide or mixture of oxides having a higher proportion of oxygen than is the case with nickelous oxide, NiO. J. J. Berzelius,[2] O. Brunck, and T. Vorster reported nickelic oxide to be formed when finely-powdered nickel nitrate is heated below redness with constant stirring; J. L. Proust, and H. Moissan, by heating nickel carbonate in air; O. Brunck, and F. Glaser, by heating nickelous hydroxide in air at 255° to 300°; and A. Mailfert, by the action of ozone on the oxide, hydroxide, or sulphide.

According to A. Peter, the dehydration of the hydrated oxide shows a definite arrest corresponding with the monohydrate, $Ni_2O_3H_2O$. The dihydrate, $Ni_2O_3.2H_2O$, was reported by N. W. Fischer to be formed at the anode during the electrolysis of a soln. of a nickel salt; and W. Wernicke obtained it in an analogous manner with a soln. of potassium nickel tartrate. H. Riesenfeld, and A. Thiel and A. Windelschmidt said that the dihydrate is formed when the tetrahydrate is heated to 200° to 220°. K. A. Hofmann and H. Hiendlmaier found that when potassium is burned on a nickel trough, a mixture of yellowish-brown potassium tetroxide and long, black prisms is obtained. When water is added to this product, the potassium tetroxide is decomposed into oxygen and potassium hydroxide and a black, crystalline powder subsides, which, when washed and dried, consists of raven-black, metallic prisms of the compound, $Ni_2O_5H_4$; the latter oxidizes organic substances readily. It is probably nickelous pernickelite, $NiO_2.NiO.2H_2O$. Nickelosic hydrate, $Ni_3O_4.2H_2O$, is formed a very dark brown hexagonal crystalline when sodium peroxide is fused with nickel in a nickel crucible. The crystals are washed with hot water until the washings give no reaction with phenolphthalein —this takes a long time. The crystals are then dried and magnetted to remove metallic nickel. They dissolve slowly in acids, forming nickelous acids, with hydrochloric acid, chlorine is evolved; with sulphuric and nitric acids, oxygen. The compound does not decompose at 130°, but at 140° it begins to lose water; the water is driven off at 240° and the residue is very hygroscopic, but no hydrate is formed under these conditions. According to J. L. Proust, O. Brunck, and J. L. Lassaigne, the *trihydrate*, $Ni_2O_3.3H_2O$, is formed when nickelous oxide, hydroxide, or carbonate, suspended in water, is treated with chlorine, $3NiO+Cl_2=NiCl_2+Ni_2O_3$; J. L. Proust, and R. Böttger prepared it by warming nickelous oxide or carbonate with an aq. soln. of bleaching powder; H. Demarçay used sodium hypochlorite as oxidizing agent; A. J. Balard, O. Popp, and N. C. Nag used bromine. Nickelous oxide can also be oxidized to what was reported to be

this hydrate by sodium hypochlorite or bromine (A. Carnot, O. R. Howell); potassium hypochlorite or hypobromite (F. Meidert, and G. Schröder); or bromine (R. Fischer, and E. D. Campbell and P. F. Trowbridge). G. Wicke found that when nickelous hydroxide is allowed to stand in an atmosphere of sulphur dioxide, or when shaken in air with an alkaline soln. of sodium sulphite, it is oxidized to trihydrated nickelic oxide, and some ozone is formed; whilst C. F. Schönbein noted that nickelous hydroxide on standing exposed to air, forms a higher oxide which liberates iodine from potassium iodide. D. Bhaduri and P. Ray found that nickel hydroxide is not readily oxidized by potassium ferricyanide to a higher oxide.

C. Tubandt and W. Riedel observed that the hydrated nickelic oxide is peptized to a colloidal soln. by acetic, citric, and tartaric acids; and N. Jermolenko, by dil. hydrochloric acid. The trihydrate was reported by J. M. Merrick, and C. Thieme-Wiedtmarckter, to be formed at the anode during the electrolysis of a soln. of nickel acetate; by Nya Akkumulator Aktiebolaget Jungner, C. Tubandt, F. Förstar, W. Wernicke, A. Coehn and M. Gläser, H. Riesenfeld, and J. Zedner, by the electrolyses of alkaline soln. of nickel salts in the presence of alkali tartrates or acetates; and by W. Pfanhauser, by the electrolysis of a soln. of ammonium nickel sulphate (*q.v.*). Its formation in the nickel accumulator was discussed by F. Förster, R. Gahl, K. Elbs, A. L. Marsh, and A. E. Kennelly. J. Zedner found the trihydrate to be stable in an atmosphere of which the press. of water vapour is less than 3 mm. According to H. Riesenfeld, and A. Thiel and A. Windelschmidt, the *tetrahydrate*, $Ni_2O_3.4H_2O$, is formed at the nickel or platinum anode during the electrolysis of a soln. of a nickel salt. J. Zedner said that the *hexahydrate*, $Ni_2O_3.6H_2O$, is the stable phase when the vap. press. of water is above 3 mm. press., and below that, the trihydrate is the stable phase. T. Carnelley and J. Walker observed no signs of discontinuity in the heating curves of hydrated nickelic oxide. R. W. Cairns and E. Ott observed the existence of only the monohydrate and the dihydrate.

The properties of nickelic oxide and its hydrates.—Anhydrous nickelic oxide is said to be a black powder; the dihydrate, a brownish-black crystalline powder, which, according to K. A. Hofmann and H. Hiendlmaier, consists of jet-black, elongated, striated prisms with a metallic lustre. G. L. Clark and co-workers found that the X-radiograms of nickelic oxide showed that it is a mixture of nickel monoxide and dioxide. Similar results were obtained by V. M. Goldschmidt and co-workers, M. le Blanc and R. Müller, and G. Lunde. S. B. Hendricks and co-workers doubt if nickelic oxide has ever been prepared. M. le Blanc and H. Sachse, D. K. Goralevitsch, and H. Rheinboldt discussed the structure of nickelic hydroxide. J. Zedner said that the trihydrate is a black powder which under water appears to be dark brown. The tetrahydrate is described as a brownish-black precipitate. W. Herapath gave 4·846 for the sp. gr. of the anhydrous oxide; L. Playfair and J. P. Joule, 4·814; and W. Wernicke gave 2·744 for the sp. gr. of the dihydrate. W. J. Russell said that when the anhydride is heated it glows with the evolution of oxygen to form nickelous oxide. When heated 14 days between 160° and 180° in dry ammonia, the hydrate loses 17·25 per cent. of water ($2H_2O$=16·08 per cent.). H. Riesenfeld observed that the tetrahydrate loses two mols. of water at 200° to 220°; and F. Glaser observed that at 109° to 112°, the dihydrate forms nickelous hydroxide. According to A. Peter, and G. F. Hüttig and A. Peter, the dehydration curves of two samples of hydrated nickelic oxide are shown in Fig. 321. There is a definite *monohydrate*, $Ni_2O_3.H_2O$, with a decomposition temp. of 138°, at 10 mm. press. The monohydrate breaks up irreversibly in accord with the equation: $2(Ni_2O_3.H_2O)=4NiO+2H_2O+O_2$. For proportions of water in excess of the monohydrate, the dehydration process is reversible. There is no evidence of the existence of a definite hydrate above the monohydrate either on the dehydration curves, or amongst the X-ray spectral lines. J. Thomsen gave for the heat of formation, $(2Ni,3O,3H_2O)$=120·38 Cals.;

and $(2Ni(OH)_2,3O,H_2O)=-1·3$ Cals. F. Giordani and E. Mattias found that the heats of dissolution of the peroxidized nickel oxide agree with the assumption that two oxides are formed—either Ni_3O_4 and Ni_4O_5, or Ni_2O_3 and Ni_3O_4. They also calculated for the reactions in the nickel accumulator: $Ni_2O_3+Fe+3H_2O=2Ni(OH)_2+Fe(OH)_2+65·215$ Cals., and $Ni_3O_4+Fe+4H_2O=3Ni(OH)_2+Fe(OH)_2+63·95$ Cals. The first reaction leads to a value of 1·338 volts, and the second to 1·311 volts for the potential of the cell; both of their values are rather lower than the measured voltage, 1·36. J. S. Hunter studied the photoelectric properties; J. Shearer, the L-series of the X-ray spectrum; and J. Vrede, the oxide as a radiodetector. K. Friederich gave $5·2\times10^8$ ohms per sq. mm. for the resistance of nickel oxide. F. Streintz observed that the compressed powder is to be regarded as a non-conductor of electricity. J. Zedner said that a paste made of the trihydrate on platinum in a 25 per cent. soln. of potassium hydroxide has a potential of 1·1 volt; and when used as anode a potential of 1·4 volt. If a nickel plate is oxidized by chlorine, in a soln. of potassium hydroxide, it gives an e.m.f. of 1·74 to 1·79 volt against zinc. A. H. Barnes studied the X-ray spectrum. W. Pfanhauser found that the electrode potentials of nickelic hydroxide in N-$NiSO_4$ and N-$(NH_4)_2Ni(SO_4)_2$ are, respectively, $-1·135$ and $-1·152$ volts. S. Veil found the mol. coeff. of magnetization rises as nickelic hydroxide is repeatedly dissolved and reprecipitated, until it attains a maximum value. W. Klemm and K. Hass studied the subject.

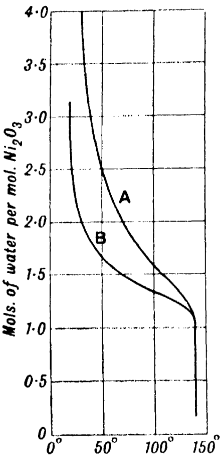

FIG. 321.—Dehydration Curves of Hydrated Nickelic Oxide.

According to T. Vorster, when anhydrous nickelic oxide is gently heated in hydrogen or dry ammonia, it becomes greyish-yellow, and when heated to a still higher temp. it forms yellowish nickelous oxide, and finally the metal. H. Salmang observed that the oxide is unstable in aq. soln., but is stable in fusions. W. Müller said that the trihydrate in **hydrogen** begins to give off oxygen at 150°, the action then ceases and begins again at about 360°. G. Gallo said that the first stage of the reduction, $Ni_2O_3+H_2=2NiO+H_2O$, begins at 92° to 95°, and the reduction of the nickelous oxide begins at 118° to 120°. In the presence of moisture, 20 mm. press., the reduction of nickelic oxide begins at 120° to 122°, and requires a longer time for its completion than with the dry gas. F. Glaser's results were not sensitive enough to detail the commencement of the reduction. W. N. Ipatéeff, and L. Brunel and P. Woog tried nickelic oxide as a catalyst in hydrogenations. S. Hauser found that oxide begins to evolve oxygen at 106° to 118°; and F. Glaser observed that the nickelic oxide forms nickelosic oxide in hydrogen at 188°; W. N. Ipatéeff said that the reduction of nickelic oxide to the metal at ordinary press. begins at 190° to 200°, at 100 atm. decomposition is measurable at 168°. Nickelic oxide was found by O. Brunck to give no evidence of any alteration when heated in **oxygen**; but it gives ozone at a higher temp. in oxygen. H. Demarçay observed that when the trihydrate is boiled with **water** or with water containing a trace of acid, oxygen is given off. T. Bayley observed that the anhydrous oxide in contact with **hydrogen dioxide** causes a vigorous evolution of oxygen, and G. Watson observed no evidence of the formation of a peroxide during the reaction. The reaction with the hydrate was studied by K. A. Hofmann and H. Hiendlmaier. J. L. Proust, G. C. Winkelblech, and H. Riesenfeld said that the hydrate dissolves in **hydrochloric acid** with the evolution of chlorine. As emphasized by E. Dufau, and C. Tubandt and W. Riedel, nickelic oxide has no acidic properties, and does not form *nickelic salts*. C. Wicke observed that the trihydrate is converted into a higher oxide, Ni_4O_7, by the action of **sodium hypochlorite** at ordinary temp. O. Brunck found that a mixture of nickelic oxide and **potassium chlorate** reacts

so violently at 300° that the mixture becomes red-hot. Some ozone is formed. S. M. Tanatar found that it dissolves in **sulphuric acid** with the evolution of oxygen. According to J. L. Proust, and G. C. Winkelblech, anhydrous nickelic oxide dissolves in aq. **ammonia** with the liberation of nitrogen; T. Vorster also observed the same phenomenon with the hydrate. S. M. Tanatar found that the anhydride dissolves in **nitric acid** with the evolution of oxygen. C. Wicke found that the moist hydrate is reduced to nickelous oxide by **sodium arsenite.**

K. Iwase and M. Fukusima found that the reduction of the oxide by **carbon** is promoted by the presence of lime. I. L. Bell noted that **carbon monoxide,** free from cyanogen, reduces nickelic oxide to the metal, and the reaction is attended by the separation of much carbon. When heated to 400° in a current of **carbon dioxide,** nickelic oxide yields only a trace of ozone. W. P. Yant and C. O. Hawk studied its catalytic effect in the oxidation of **methane.** T. Vorster found that hydrated nickelic oxide is reduced to nickelous oxide when it is heated with **alcohol** in a sealed tube to 150°. G. C. Winkelblech found that a cold, aq. soln. of **oxalic acid** forms green nickel oxalate with the evolution of carbon dioxide. According to S. R. Benedict, a solution of nickelic acetate can be obtained by dissolving freshly-precipitated nickelic hydroxide in well-cooled, 90 per cent. **acetic acid.** This soln. gradually undergoes reduction in the cold, instantaneously on warming, and is immediately reduced by all reducing agents. Similar soln. can be obtained by the action of **citric** and **tartaric acids** on nickelic hydroxide. When freshly-precipitated nickelic hydroxide is treated with a nearly sat. soln. of **potassium hydrosulphate,** a soln. is obtained which is a powerful oxidizing agent, and it is supposed to contain either a simple or complex nickelic sulphate. C. Tubandt and W. Riedel observed that S. R. Benedict's nickelic acetate is really a colloidal soln. of nickel dioxide; and his nickelic sulphate is a soln. of nickelous sulphate containing the perphosphoric acid of J. Schmidlin and P. Massini (**8**. 50, 29); the red colour is due to manganese present as one impurity. Hydrated nickelic oxide was found by E. Donath rapidly to form a blue soln. when treated with **glycerol,** and soda-lye, or with glycerol, aq. ammonia, and ammonium chloride. The reaction is so slow with hydrated cobaltic oxide that it can be utilized to detect nickel in the presence of cobalt. K. A. Hofmann and H. Hiendlmaier observed that hydrated nickelic oxide has a strong oxidizing action on **organic substances**—*e.g.*, **alcohol** is converted in the presence of sulphuric acid into aldehyde; and the oxide is reduced by **cellulose.** O. Mai and M. Silberberg observed that the hydrate is rapidly converted by a dil. soln. of **potassium cyanide** into a gel. H. Demarçay said that the hydrate can be boiled with a soln. of **alkali hydroxide** without decomposition, but G. Schröder said that boiling potash-lye converts it into nickelosic oxide with the evolution of oxygen. S. M. Tanatar found that when warmed with a soln. of **barium hydroxide** containing some potassium permanganate, oxygen is evolved, and the soln. is decolorized—*vide infra*, nickel dioxide.

Intermediate oxides.—The analyses of anhydrous nickelic oxide by I. L. Bell, T. Vorster, J. L. Lassaigne, and E. Rothoff agree with the formula Ni_2O_3; the analyses of the dihydrate by W. Wernicke, and H. Riesenfeld agree with $Ni_2O_3.2H_2O$; that of the trihydrate by G. C. Winkelblech agree with $Ni_2O_3.3H_2O$; and that of the tetrahydrate by H. Riesenfeld, with $Ni_2O_3.4H_2O$. The individuality of the oxide thus appears to be fairly well established. Doubts, however, have been raised. K. A. Hofmann and H. Hiendlmaier—*vide supra*—suggested that the dihydrate does not contain tervalent nickel in accord with $Ni_2O_3.2H_2O$, but rather quadrivalent nickel in accord with $NiO.NiO_2.2H_2O$, so that the alleged nickelic oxide is nickelous pernickelite, where the term is uniform with the permanganites and perferrites. I. Bellucci and E. Clavari said that, unlike cobalt, nickel does not form an oxide of the type $R_2'''O_3$, and that the oxide previously regarded as Ni_2O_3 is a mixture of variable proportions of NiO and NiO_2. This conclusion is in accord with the evidence furnished by the X-radiograms—*vide supra*. I. Bellucci and E. Clavari based their opinion on the oxidation of nickel sulphate in alkaline

soln. by various oxidizing agents under various conditions of temp. and dilution. They found :

(1) Any one oxidizing agent yields, both at the ordinary temperature and on heating, products giving the same value for the ratio nickel : oxygen, but at 0° the proportion of oxygen is much higher. (2) The degree of oxidation of the nickel depends on the nature of the oxidizing agent and on the rapidity of the oxidation, the lowest numbers being obtained when the precipitate is left for a long time in contact with excess of the oxidizing solution. (3) None of the oxidizing agents employed led to the formation of an oxide having the formula Ni_2O_3. (4) On oxidation with bromine in presence of excess of potassium carbonate at 0° and washing the precipitate with concentrated potassium carbonate solution, the ratio of nickel to oxygen was found to have the value 10 : 19·07 ; this is in good agreement with the numbers 10 : 20 required by the oxide NiO_2, the existence of which has been assumed by E. Dufau. This oxide readily loses oxygen, forming substances which vary in composition with the conditions, and to which no definite formulæ can be given. (5) When nickel dioxide loses oxygen, no arrest occurs at the stage Ni_2O_3, which may, however, represent a relatively stable compound ; on drying over calcium chloride at 100°, it passes always into compounds for which the ratio of Ni : O is in some cases approximately 10 : 14 and in others 10 : 13.

In preparing nickelosic oxide by the action of fused sodium on nickel, I. Bellucci and S. Rubegni assumed that a *sodium nickelous pernickelite*, $Na_2O.NiO.2NiO_2$, or $Na_2Ni(NiO_3)_2$, is formed ; when this product is washed with boiling water, it hydrolyzes to form nickelosic oxide, $2NiO.NiO_2.2H_2O$, whilst the *potassium nickelous pernickelite*, $K_2O,NiO.NiO_2$, of K. A. Hofmann and H. Hiendlmaier, yields *nickelous pernickelite*, $NiO.NiO_2.2H_2O$.

D. K. Goralevitsch made a series of experiments on the nickel oxides, and he considered that he had established the existence of NiO, Ni_3O_4,Ni_2O_3, and of NiO_2, as well as of a number of other oxides. The evidence, however, admits of other conclusions. He found that

(1) Nickel oxides, ranging from $NiO_{1\cdot81}$ to $NiO_{1\cdot36}$, have been prepared by the electrolysis of a strongly alkaline soln. of sodium pyrophosphate with nickel in suspension—the oxides ranged from 67 to 73 per cent. of nickel ; 27 to 34 per cent. of oxygen ; no water of hydration ; 6 to 16 per cent. of active oxygen liberated by the action of water at 50° ; and 7 to 16 per cent. of active oxygen liberated by the action of sulphuric acid. These oxides furnish nickelous oxide by thermal decomposition. (2) Nickel oxides, ranging from $NiO_{1\cdot89}$ to $NiO_{1\cdot36}$, were prepared by the electrolysis of alkaline soln. from which chlorine was liberated electrolytically, and which had hydrated nickelous oxide in suspension—the oxides ranged from 66 to 73 per cent. of nickel, and 27 to 34 per cent. of oxygen ; 5 to 16 per cent. of active oxygen liberated by the action of water at 50° ; and 7 to 16 per cent. of active oxygen liberated by the action of sulphuric acid. (3) Nickel oxides, ranging from $NiO_{1\cdot89}$ to $NiO_{1\cdot36}$, were obtained by the oxidation of nickel salts, including chlorides, by the action of potassium persulphate in alkaline soln. The products contained 9 to 10 per cent. of H_2O, or, neglecting water, 66 to 73 per cent. of nickel, 27 to 34 per cent. of oxygen ; 7 to 16 per cent. of active oxygen liberated by the action of water at 50° ; and 7 to 16 per cent. of oxygen liberated by the action of sulphuric acid. (4) Nickel oxides, ranging from $NiO_{1\cdot81}$ to $NiO_{1\cdot43}$, were obtained by the oxidation of nickelous oxide by gently heating it with dry potassium nitrate. The products contained 67 to 72 per cent. of nickel ; 28 to 34 per cent. of oxygen ; 8 to 15 per cent. of active oxygen liberated by the action of water at 50° ; and 7 to 15 per cent. of active oxygen liberated by the action of sulphuric acid. (5) When potassium chlorate is employed in place of the nitrate, the products, ranging from $NiO_{1\cdot89}$ to $NiO_{1\cdot57}$, contained 66 to 70 per cent. of nickel ; 30 to 34 per cent. of oxygen ; 11 to 16 per cent. of active oxygen liberated by the action of water at 50° ; and 10 to 17 per cent. of active oxygen liberated by the action of sulphuric acid. (6) Nickel oxide, $NiO_{1\cdot57}$, obtained by heating the nitrate or carbonate, gave products with 71 per cent. of nickel ; 29 per cent. of oxygen ; and 9·5 to 10 per cent. of active oxygen liberated by the action of sulphuric acid.

An indefinitely large number of intermediate compounds has been reported between NiO and NiO_2. In analogous cases, where suitable investigations have been made, most of the intermediate stages have been shown to be solid soln. of one oxide in the other ; or else the products represent a reaction arrested at different stages—either the oxidation of nickel monoxide to dioxide, or the reduction of nickel dioxide to monoxide. As G. Schröder said of those reported up to his time, their chemical individuality is doubtful.

D. K. Goralevitsch inferred the existence of the following complex oxides of low stability: Ni_5O_9, or $NiO.4NiO_2$; Ni_6O_{11}, or $NiO.5NiO_2$; Ni_3O_5, or $NiO.2NiO_2$; Ni_9O_{17}, or $NiO.8NiO_2$; Ni_7O_{12}, or $2NiO.5NiO_2$; Ni_8O_{15}, or $NiO.7NiO_2$; Ni_5O_8, or $2NiO.3NiO_2$; $Ni_{11}O_{17}$, or $5NiO.6NiO_2$; Ni_9O_{16}, or $2NiO.7NiO_2$; Ni_7O_{13}, or $NiO.6NiO_2$; Ni_3O_5, or $Ni_2O_3.NiO_2$, or $NiO.2NiO_2$; Ni_8O_{13}, or $3Ni_2O_3.2NiO_2$, or $3NiO.5NiO_2$; Ni_5O_7, or $3NiO.2NiO_2$; Ni_2O_3, or $NiO.NiO_2$; $Ni_2O_3.H_2O$, or $NiO.NiO_2.H_2O$; Ni_3O_4, or $2NiO.NiO_2$, but he is following a wrong track. T. Bayley reported Ni_3O_5 to be formed as a black powder by the action of hypochlorites on a soln. of a nickel salt. Ni_4O_7 was reported by G. C. Winkelblech, and C. Wicke to be formed by the action of sodium hypochlorite on hydrated nickelic oxide; Ni_5O_7, by G. Schröder by the action of bromine on nickel salt soln.; and $Ni_8O_{11}.9H_2O$ reported by T. Bayley to be produced by the action of water on Ni_3O_5. C. R. A. Wright and A. P. Luff reported $Ni_9O_{11}.12H_2O$ to be formed by the action of hypochlorites on a soln. of a nickel salt, and they added that reduction with hydrogen begins at 65°, with carbon at 145°, and with carbon monoxide at 30°; and that the evolution of oxygen begins at 145°. D. K. Goralevitsch gives an array of constitutional formulæ for the alleged compounds.

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§ 12. The Higher Oxides of Nickel

In 1896, E. Dufau[1] reported the formation of a salt of **nickel dioxide,** or *nickel peroxide*, NiO_2, namely, barium dipernickelite, $BaO.2NiO_2$. H. Schulze observed that when nickel chloride, bromide, or iodide is dropped into molten potassium chlorate, oxidation takes place and a mixture of nickel dioxide and monoxide is formed, and similarly when nickel nitrate or chlorate is gently heated. These products were formerly regarded as nickelic oxide, but the evidence indicates that they are indefinite mixtures of nickel dioxide and monoxide. I. Bellucci and E. Clavari obtained nickel dioxide, contaminated with more or less monoxide, by the action of persulphate, hypochlorites, hypobromites, bromine, or anodic chlorine on nickel monoxide or hydroxide suspended in alkaline soln. The degree of oxidation depends on the temp., and the time of exposure to the oxidation. A higher degree of oxidation is obtained with soln. made alkaline with alkali carbonates rather than with alkali hydroxides; and by washing the precipitates with a dil. soln. of alkaline carbonate rather than with water. If n denotes the at. proportion of oxygen combined with nickel in NiO_n, the values of n with different oxidizing agents, at different temp., were:

	Hot solutions	16° (*circa*)	0°
Persulphates	1·46 to 1·48	1·36 to 1·642	1·64 to 1·645
Hypochlorites	1·48 to 1·58	1·56 to 1·57	1·756 to 1·791
Bromine	1·54 to 1·079	1·638 to 1·746	1·828 to 1·907
Hypobromites	1·47 to 1·70	1·64 to 1·68	—
Anodic chlorine	—	1·52 to 1·56	—

O. R. Howell found that hypochlorites free from alkali react far more slowly with soln. of nickel sulphate than they do in the presence of alkalies. With an excess of alkali, the precipitated nickel hydroxide is oxidized, and the oxidation

is quantitative up to the nickelic oxide stage, but owing to the catalytic decomposition of nickel dioxide, larger proportions of hypochlorite yield only a small proportionate increase in the oxidation. With sodium carbonate, hypochlorites oxidize the precipitated nickel carbonate, but the liberated carbon dioxide yields nickel hydrocarbonate so that precipitation is not complete. The oxidized precipitate is very unstable and evolves oxygen even when it is suspended in the soln. at ordinary temp. The decomposition proceeds beyond the nickelic oxide stage, and the speed of the decomposition is retarded by alkalies. There is an increase in the progress of the oxidation with an increase in the concentration of the reacting soln., presumably owing to the protective effect of the alkalies. The oxidation does not progress so far at higher temp. because of the increased rate at which the precipitate decomposes. Nickel dioxide decomposes directly to the hydrated monoxide without the production of nickelic oxide; nickelic oxide is not produced as an intermediate stage. At the b.p. of the soln. nickel dioxide decomposes rapidly, and nickelic oxide slowly, so that it is possible to estimate the relative proportion $Ni_2O_3 : NiO_2$ in a green precipitate. Nickelous hydroxide is oxidized simultaneously to nickelic oxide and nickel dioxide, and nickelic oxide is not an intermediate stage in the formation of the dioxide. The precipitate consists of a mixture of the three oxides—NiO, Ni_2O_3, and NiO_2; but with sufficient hypochlorite, all the monoxide can be oxidized to the other two oxides. Nickelic oxide is not oxidized to the dioxide, so that the dioxide represents the limit set to the oxygen content of the precipitate. It is assumed that the oxidation proceeds *viâ* the complex $NiO_2.3NiO$, thus:

$$4NiO \rightarrow NiO_2{\cdot}3NiO \lessgtr \begin{matrix} NiO_2.NiO \rightarrow nNiO_2 \\ Ni_2O_3 \quad \rightarrow mNi_2O_3 \end{matrix}$$

With just sufficient alkali for precipitation, the oxygen supplied by the hypochlorite first enters almost wholly as peroxide and then as sesquioxide. This is attributed to the formation and subsequent oxidation of a complex. With increasing amount of alkali for precipitation, the fraction of nickel precipitated as peroxide increases and is proportional to the adsorption of the alkali. This is attributed to the stabilizing effect of the alkali by adsorption. The reaction was studied by E. Chirnoaga, and by M. le Blanc and R. Müller—*vide* cobalt dioxide. The increased yield of the higher oxide with more conc. soln. of potassium carbonate, in the oxidation with bromine, is attributed to the great degree of dispersion of the nickelous hydroxide.

Nickel dioxide is supposed to be formed in the nickel oxide accumulator (*q.v.*) during the anodic oxidation of nickel oxide in alkaline soln. The subject was discussed by F. Förster, H. Riesenfeld, C. Tubandt and W. Riedel, J. Zedner, A. L. Marsh, and A. E. Kennelly. C. Tubandt and W. Riedel observed that the electrolysis of alkali carbonate soln. containing nickel, between nickel plates, using a diaphragm, yields a dark soln. which contains only the colloidal dioxide.

G. L. Clark and co-workers found that the X-radiograms of the forms of nickel dioxide gave no diffraction lines; this indicates an amorphous structure. If nickelic oxide be in truth a mixture of nickel dioxide and monoxide—and there is now very little doubt about this—then most of the chemical properties assigned to nickelic oxide should be transferred to nickel dioxide. The dioxide loses oxygen when dried in air or over desiccating agents, and furnishes a series of indefinite mixtures, $NiO : NiO_2$. H. Moissan said that the reduction by hydrogen begins at about 190°. The dioxide burns in fluorine. The dioxide decomposes hydrogen dioxide with the evolution of oxygen; it dissolves in acids, forming nickelous salts; with hydrochloric acid it yields chlorine; with hydrogen sulphide it forms water and nickel monosulphide; with sulphurous acid it forms a sulphite and dithionate; and with sulphuric acid, oxygen is given off and nickelous sulphate is formed. According to C. Tubandt and W. Riedel, when a fine, aq. suspension of nickel dioxide is treated with dilute sulphuric acid, a soln. is obtained which

liberates iodine from potassium iodide, and decolorizes permanganate to some extent. These reactions are not due, as suggested by S. M. Tanatar, to the formation of hydrogen dioxide, which is not present even in traces. It is assumed that the liberation of iodine is due to the formation of persulphuric acid, or of Caro's acid, even in the dil. sulphuric acid used. The decoloration of the permanganate is only apparent, the colour being masked by the green colour of the nickel soln. C. Tubandt and W. Riedel observed that strongly-cooled, alcoholic soln. of acids yield with nickel dioxide dark red, colloidal soln. According to C. Tubandt and W. Riedel, phosphoric acid forms stable colloidal soln. S. M. Tanatar showed the formation of hydrogen dioxide when nickel dioxide acts on a soln. of hydrocyanic acid in the presence of potassium cyanide, and C. Tubandt and W. Riedel added that the hydrogen dioxide is not formed from the nickel peroxide, however, but by the auto-oxidizing action of the complex nickel cyanides formed. This is supported by the fact that nickel hydroxide or any nickel salt may be used in place of the dioxide. S. M. Tanatar, however, showed that a soln. of nickel peroxide in sulphuric acid contains, not only persulphuric acid, but also hydrogen peroxide. The greatest amount of hydrogen peroxide is produced when the nickel peroxide is dissolved in a soln. of hydrogen cyanide containing potassium cyanide; this cannot be due to the auto-oxidizing action of the nickel-cyanogen complex produced, since neither nickel hydroxide nor nickel salts, when free from cobalt, give rise to hydrogen peroxide under the same conditions. The different results obtained by C. Tubandt and W. Riedel were probably due to the fact that the nickel peroxide used by them contained cobalt, it being well known that hydrogen peroxide is produced during the oxidation of potassium cobalto-cyanide.

G. Pellini and D. Meneghini prepared *hydrated* nickel dioxide, $NiO_2.nH_2O$, by adding to a dil. soln. of nickel chloride, cooled to $-50°$, an equal vol. of 30 per cent. hydrogen dioxide, and finally an alcoholic soln. of potassium hydroxide. The product was washed several times with cold alcohol, and then with ether. The greenish-grey powder is stable in air. The pure dioxide has not been prepared, but it has been obtained as close to NiO_2 as $NiO_{1\cdot98}$. The same dioxide was obtained by the action of hydrogen dioxide on free nickelous hydroxide, but the reaction is very slow. The green dioxide so obtained is rather different from that obtained by I. Bellucci and E. Clavari. Since the green product gives all the reactions of hydrogen dioxide, G. Pellini and D. Meneghini suggest that their product has the constitution

$$\mathrm{Ni}{<}^{\mathrm{O}}_{\mathrm{O}}\,; \quad \text{and} \quad \mathrm{Ni}{\lll}^{\mathrm{O}}_{\mathrm{O}}$$

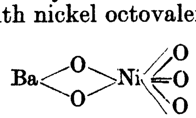
is given for the constitutional formulæ of the compound described by I. Bellucci and E. Clavari. The constitution was also discussed by S. M. Tanatar, C. Tubandt and W. Riedel, D. K. Goralevitsch, and H. Baubigny. According to R. Müller, and M. le Blanc and H. Sachse, nickel oxide can take up oxygen without forming a chemical compound. The product, owing to its high degree of dispersion, does not show a definite space-lattice when X-radiograms are taken. F. Göbel studied the reduction with carbon monoxide.

Pernickelites.—As indicated above, K. A. Hofmann and H. Hiendlmaier reported **potassium nickelous pernickelite,** $K_2O.NiO.NiO_2$—possibly an oxypernickelite, $K_2NiO(NiO_3)$—to be formed when potassium burns on a nickel plate. The black, hygroscopic, prismatic crystals are decomposed slowly by exposure to a moist atmosphere or to water, when nickelous pernickelite, $NiO.NiO_2.2H_2O$, or $Ni(NiO_3).2H_2O$, is formed. I. Bellucci and S. Rubegni reported **sodium nickelous pernickelite,** $Na_2O.NiO.2NiO_2$, or $Na_2Ni(NiO_3)_2$, to be formed by the method used in the preparation of hydrated nickelosic oxide (*q.v.*), and separating the products of the reaction by flotation with methylene iodide. E. Dufau could not prepare **calcium pernickelite,** nor **strontium pernickelite,** but he obtained **barium**

pernickelite, $BaO.2NiO_2$, by heating an intimate mixture of nickelic oxide (85 parts), barium oxide (155 parts), or barium carbonate (200 parts), surrounded by barium oxide, in an electric arc furnace for 10 mins. The grey mass has a crystalline fracture, but it soon disintegrates on exposure to air; and, when rapidly treated with cold water, levigated, and finally washed and levigated with alcohol, it yields small, brilliant, dark coloured crystals which are greenish-brown when powdered. The sp. gr. is 4·8 at 20°, and the hardness is a little over 4. The salt is not stable. Cold water attacks the crystals slowly, and hot water rapidly. Hydrofluoric acid dissolves them with effervescence, and hydrochloric acid with evolution of chlorine; nitric acid and ammonia also dissolve and decompose them. Chlorine, bromine, and iodine attack the nickelite at a red-heat, with formation of halogen salts of the metals, but oxygen has no action at bright redness. Sulphur, a little above its m.p., converts the nickelite into sulphides with incandescence. Hydrogen fluoride and hydrogen chloride decompose it at a red heat, but fused neutral oxidizing agents are without action on it. J. J. Berzelius prepared what he called *Nickeloxydul-magnesia* by precipitation with aq. ammonia from a mixed soln. of nickel and magnesium salts. E. Dufau could not prepare **magnesium pernickelite.** K. A. Hofmann and H. Hiendlmaier obtained **nickelous pernickelite** as indicated above, and the alleged nickelic oxide (*q.v.*) is supposed to be this pernickelite.

The nickelates and pernickelates.—The nickelates are salts of the hypothetical **nickel trioxide,** NiO_3. D. K. Goralevitsch fused nickel monoxide with potassium nitrate or chlorate in the presence of an excess of alkali hydroxide, and obtained a bright green **potassium nickelate,** K_2NiO_4, which is unstable and decomposes with the evolution of oxygen. The nickelate is soluble in water. The corresponding **sodium nickelate,** Na_2NiO_4, was prepared in an analogous manner. It is hygroscopic, and, like the potassium salt, unstable. By treating the freshly-prepared soln. of the alkali nickelates with alkaline earth salts the corresponding **alkaline earth nickelates** are formed. They resemble the corresponding ferrates, but are more stable. In aq. soln., the alkali ferrates decomposed in 20 to 30 mins., but the alkali nickelates decomposed under similar conditions in a few hours. The green soln. of potassium nickelate decomposed completely with the liberation of grey nickelous oxide in 24 hrs.

In preparing the alkali nickelates, there is simultaneously formed a small proportion of a greyish-green substance which liberates oxygen when treated with hot water, or with nitric or hydrochloric acid; it dissolves without decomposition in hot, conc. hydrochloric acid, but separates from the acid on cooling. The product is **potassium pernickelate,** K_2NiO_5. Large yields of the pernickelate can be obtained by fusing in a silver vessel a mixture of nickel monoxide and potassium nitrate, and adding potassium dioxide to the hot, fused product. The mixture is heated again, cooled, powdered, and washed with ice-water on a filter-paper. The corresponding **sodium pernickelate,** Na_2NiO_5, was obtained in an analogous manner; and likewise with **barium pernickelate,** $BaNiO_5$. Unlike the sodium and potassium salts, barium pernickelate is not decomposed by hot water, or by heating it to redness, but it is decomposed by sulphuric and nitric acids, with the liberation of oxygen; when it is treated with conc. hydrochloric acid, and heated, chlorine is evolved. The products obtained by the above fusion processes are therefore mixtures. When repeatedly washed with dil. acetic acid, the residue on the filter-paper is $BaO_2.NiO_3$, with nickel octovalent:



According to D. K. Goralevitsch, when sodium, potassium, or barium pernickelate is treated with conc. hydrochloric acid, a green precipitate of **nickel hemipentoxide,** Ni_2O_5, is said to be formed; it is unstable and readily decomposes into nickel monoxide and oxygen. When nickel hemipentoxide is heated with

conc. hydrochloric acid, a white **nickel tetroxide,** NiO_4, is formed, and it decomposes on exposure to air into nickelous oxide and oxygen. A. Hollard found that when a solution of nickel (0·05 grm. in 300 c.c.) containing chromic acid and alkali pyrophosphate is electrolyzed at 70°, using a current of 0·1 ampere for 54 hrs., the tetroxide NiO_4 was deposited.

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§ 13. Nickel Fluorides

Nickel fluoride is obtained when a soln. of the carbonate in hydrofluoric acid is evaporated. C. Poulenc [1] prepared **nickel fluoride,** NiF_2, by melting an excess of ammonium fluoride with anhydrous nickel chloride, and when the mass is cold extracting it with boiling alcohol to remove the ammonium chloride. The yellow ammonium nickelous fluoride is heated to redness in an inert gas, and there remains pulverulent nickelous fluoride, which, when heated, between 1200° to 1300°, in dry hydrogen fluoride, becomes crystalline.

Nickel fluoride crystallizes in yellowish-green, elongated prisms. According to A. Ferrari, the crystals are tetragonal of the rutile type and the X-radiograms show that the lattice dimensions are a=4·710 A., c=3·118 A., and $a : c$=1 : 0·662 ; O. Ruff and E. Ascher likewise calculated 4·79. The volume of the lattice is $69{\cdot}17\times10^{-24}$ c.c., and the calculated density is 4·641. V. M. Goldschmidt and co-workers studied the subject. C. Poulenc found the sp. gr. to be 4·63. F. W. Clarke's value, 2·855 at 14°, is probably too low. W. Biltz and E. Rahlfs gave 4·60 for the sp. gr. at 25°/4°, 21·01 for the mol. vol., and 7·3 for the mol. vol. of the fluoride.

A. Rudat calculated 157,500 cals. per mol. for the heat of formation, at 300° to 500°, and for the pressure, p, of the fluoride, at 300°, 400°, 450°, and 500°, he gave $p=4{\cdot}0\times10^{-53}$, $3{\cdot}1\times10^{-44}$, $9{\cdot}1\times10^{-41}$, and $1{\cdot}1\times10^{-37}$ respectively. H. von Wartenberg gave 171·4 Cals. for the heat of formation of the fluoride in aq. soln. G. Beck studied the subject. C. Poulenc observed that the salt sublimes in hydrogen fluoride when it is heated above 1000°. E. Petersen found the heat of neutralization of $\frac{1}{2}Ni(OH)_2$ by HFaq. is 13·835 Cals. ; H. von Wartenberg and O. Fitzner gave $(Ni,F_2,Aq.)$=171·4 Cals. G. Beck studied the energy of the molecule ; G. Denigès, the absorption spectrum ; P. Henkel and W. Klemm, and R. A. Fereday, the magnetic susceptibility of the nickel fluoride.

C. Poulenc found that the fluoride is reduced to the metal when heated in hydrogen. K. Jellinek and A. Rudat studied the equilibrium $NiF_2+H_2\rightleftharpoons Ni+2HF$ approached from the hydrogen side because of the slow rate of diffusion of hydrogen

fluoride through the film of fluoride, first formed on the surface of the metal, when an approach is made from the other side. The equilibrium constants, $K=P^2_{HF}/P_{H_2}$ at 300°, 400°, 450°, and 500°, are, respectively, K=0·0033, 0·1380, 0·5495, and 2·09. A. Serres studied the magnetic properties; and B. Cabrera and A. Duperier, the effect of temp. on the magnetic susceptibility. C. Poulenc found that the fluoride is converted into oxide when heated in air. H. Schulze made observations on the subject. According to C. Poulenc, the salt is almost insoluble in water, but water vapour converts it into the black oxide, or at a higher temp., into green nickelous oxide. A. Kurtenacker and co-workers found that the solubility, S per cent. NiF_2, in water at 10° is 2·49; at 50°, 2·50; and at 100°, 2·52; and it is therefore almost independent of temperature, with the solid phase $NiF_2.4H_2O$. A. Kurtenacker and co-workers found that the solubility in per cent. by weight NiF_2, at 20°, rapidly increases with the proportion of **hydrofluoric acid** when the solid phase is $NiF_2.4H_2O$:

HF . .	0	9·25	12·39	17·46	30·10 per cent.
NiF_2 . .	2·50	7·73	10·02	11·45	13·30 ,,

O. Ruff and E. Ascher found that bromine vapour does not attack nickelous fluoride, likewise also iodine; 40 per cent. hydrofluoric acid dissolves the crystals, and on evaporation the soln. furnishes the green hydrate. According to C. Poulenc, when nickel fluoride is heated in hydrogen chloride, the fluoride is converted into chloride; the fluoride is not attacked by warm hydrochloric acid. When nickel fluoride is heated with sulphur, nickel sulphide is formed, and similarly when it is heated to redness in hydrogen sulphide. O. Ruff and E. Ascher found that at a red-heat sulphur dioxide darkens the crystals. According to C. Poulenc, the fluoride is not attacked by warm sulphuric acid. O. Ruff and E. Ascher observed that when heated in ammonia, nickel fluoride is reduced to metal. G. Gore found nickel fluoride to be insoluble in liquid ammonia. H. von Helmolt observed that the fluoride dissolves in a hot soln. of ammonium fluoride to form a complex salt. C. Poulenc observed that nickel fluoride is not attacked by warm nitric acid. O. Ruff and E. Ascher said that there is no reaction between nickel fluoride and red phosphorus, arsenic, or carbon. C. Poulenc found that nickel fluoride is insoluble in benzene, alcohol, and ether. G. Gore observed that in aq. soln. of nickel fluoride in dil. hydrofluoric acid, no nickel is deposited in the presence of silicon; but the reaction is vigorous when silicon is heated with crystals of nickel fluoride. O. Ruff and E. Ascher observed that the fluoride is only feebly attacked when it is boiled with 12 per cent. acetic acid. The fluoride reacts with crystalline silicon below redness, it also reacts vigorously when heated with sodium, magnesium, aluminium, and zinc, but not perceptibly with copper or iron. When boiled with a 33 per cent. soln. of sodium hydroxide, a green liquid is produced. C. Poulenc found that when the fluoride is heated with alkali, nickel oxide and alkali fluoride are formed.

R. H. Carter found that at 25°, 100 c.c. of the sat. aq. soln. contain 4·030 grms. of nickel fluoride. J. J. Berzelius prepared pale green crystals of what he regarded as the *dihydrate*, $NiF_2.2H_2O$, by the evaporation of a soln. of nickel carbonate in an excess of hydrofluoric acid, but the analysis of F. W. Clarke made on crystals obtained in a similar manner corresponded with the *trihydrate*, $NiF_2.3H_2O$, of sp. gr. 2·014 at 19°. N. Costachescu could not prepare the *hexahydrate*, $NiF_2.6H_2O$, or $[Ni(H_2O)_6]F_2$, but he did obtain the *tetrahydrate*, $NiF_2.4H_2O$, or $[Ni(H_2O)_4]F_2$, in pale green, rhombic octahedra by dissolving freshly-precipitated nickel hydroxide in 40 per cent. hydrofluoric acid, diluting the soln. with an equal vol. of acid, and allowing it to crystallize in vacuo over conc. sulphuric acid. W. Biltz and E. Rahlfs gave 2·219 for the sp. gr. at 25°/4°, 76·04 for the mol. vol., and 13·76 for the mol. vol. of the water. E. Petersen gave for the heat of formation $(Ni,F_2,Aq.)$ =122·8 Cals.; and for the heat of neutralization $\frac{1}{2}Ni(OH)_2+HF.Aq.$, 13·835 Cals. E. Böhm, and F. H. Edmister and H. C. Cooper, observed that if the clear soln.

of nickel hydroxide or carbonate in an excess of hydrofluoric acid be evaporated over sulphuric acid, in vacuo, **nickel hydrofluoride,** $NiF_2.5HF.6H_2O$, is formed in small, green, prismatic crystals isomorphous with the corresponding cobalt salt. The trigonal crystals of the hydrofluoride have $\alpha=112° 1'$, no perceptible cleavage, feeble and positive double refraction, and sp. gr., 2·132. B. Gossner thinks that some mistake has been made in the measurements of these crystals by E. Böhm. N. Costachescu could not prepare this hydrofluoride. According to J. J. Berzelius, if a soln. of nickel carbonate in hydrofluoric acid with the carbonate in excess, be evaporated, or if crystals of hydrated nickel fluoride be boiled with water, pale green, pulverulent **nickel oxyfluoride,** $2NiO.2NiF_2.H_2O$, is formed. G. L. Clark reported the formation of **nickel hexamminofluoride,** $NiF_2.6NH_3$, as a dark, greyish-violet powder, by the action of ammonia on anhydrous nickel fluoride; and the passage of this product with **nickel triamminofluoride,** $NiF_2.3H_2O$, on exposure to air. Both ammines have a press. of 100 mm. at 77°—*vide* the corresponding cobaltous ammines. E. Böhm found that an excess of ammonia acts on nickel fluoride, forming a soln. which, when evaporated over potassium hydroxide, in vacuo, forms an oily liquid from which pale green crystals, feebly birefringent, can be obtained. Analysis corresponds with **nickel hexamminodecafluoride,** $5NiF_2.6NH_3.8H_2O$. The salt is insoluble in cold water; decomposed by boiling water; and soluble in dil. acids. When heated in an open tube, the crystals lose water, then ammonium fluoride, and nickelous oxide remains. W. Biltz and E. Rahlfs obtained a blue oil by the simultaneous action of water vapour and ammonia on nickel fluoride; and by cooling in solid carbon dioxide a mixture of 40 c.c. of boiled alcohol with a soln. of about 6 grms. of tetrahydrated nickel fluoride in 25 c.c. of conc. aq. ammonia, there is formed **nickel aquopentamminofluoride,** $[Ni(H_2O)(NH_3)_5]F_2$, of sp. gr. 1·576 at 25°/4°; mol. vol., 126·8; mol. vol. of water, 13·6; and mol. vol. of ammonia, 18·4. The heat of formation is 11·5 Cals. per mol. of ammonia. The vap. press. curves at different temp. are indicated in Fig. 322. The numerical results for the press. p mm., are:

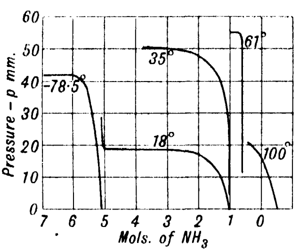

FIG. 322.—Dissociation Pressures of the Nickel Amminofluorides.

	0°	18°	35°	46·5°	61·5°
p	4·8	18·0	50·0	102·5	245·5 mm.

There is also formed green **nickel aquomonamminofluoride,** $NiF_2.H_2O.NH_3$, of sp. gr. 2·489 at 25°/4°; mol. vol., 52·71; mol. vol. of water, 13·6; mol. vol. of ammonia, 18·1. The press. at 34·5° is 10·0 mm.; at 46·5°, 22·5 mm.; and at 61°, 55 mm. The heat of formation is 12·8 Cals. per mol. of ammonia. There is also formed **nickel aquohemiamminofluoride,** $NiF_2.H_2O.\frac{1}{2}NH_3$, of sp. gr. 2·820 at 25°/4°; mol. vol. 43·69; mol. vol. of water, 13·6; and mol. vol. of ammonia, 18·2. N. Costachescu obtained from the soln. of the tetrahydrate in pyridine, azure-blue crystals of **nickelous diaquotetrapyridine fluoride,** $[Ni(H_2O)_2Py_4]F_2.H_2O$. E. Wilke-Dörfurt and H. G. Mureck obtained nickel antipyrinefluoborate, $[Ni(Antipyr)_6](BF_4)_2$.

Complex salts of nickelous fluoride.—C. Poulenc prepared anhydrous **ammonium nickel tetrafluoride,** $(NH_4)_2NiF_4$, by fusing anhydrous nickel chloride with an excess of ammonium fluoride, and washing out the ammonium chloride with boiling alcohol. The amorphous powder is soluble in water, and at a dull red-heat gives off ammonium fluoride, leaving anhydrous nickel fluoride behind. J. J. Berzelius, and R. Wagner prepared the *dihydrate*, $(NH_4)_2NiF_4.2H_2O$, from a mixed soln. of the component salts, and H. von Helmolt, by slowly evaporating a soln. of nickelous hydroxide in a hot, neutral soln. of ammonium fluoride. The pale green, or yellow crystals are isomorphous with those of the corresponding

cobalt salt; they are readily soluble in water, and the soln. does not attack glass. A. Kurtenacker and co-workers studied the equilibrium conditions in the system: NiF_2–NH_4F–H_2O at 20°, and, representing the solubility by *S* grms. of salt per 100 grms. of soln., found:

NH_4F	0	3·4	6·4	9·4	10·4	17·1	23·0	31·1	37·4
$S(NiF_2)$	2·50	1·07	0·91	0·72	0·51	0·17	0·07	0·01	0·01
Solid phase	$NiF_2.4H_2O$				$2NH_4.F.NiF_2.2H_2O$				

An analogous curve was obtained at 25°. C. Poulenc prepared anhydrous **potassium nickel tetrafluoride,** K_2NiF_4, by melting a mixture of nickel chloride and potassium fluoride. The crystals have a sp. gr. 3·27; they are readily soluble in water, but less soluble in alcohol. Cold hydrofluoric, hydrochloric, or nitric acid dissolved the salt. Aq. ammonia colours the salt blue. If heated in air, potassium fluoride volatilizes, and nickelous oxide remains. Fused alkali carbonates also furnish nickelous oxide. J. J. Berzelius, and R. Wagner reported **potassium nickel trifluoride,** $KF.NiF_2.H_2O$, to be formed as a yellow powder, or in apple-green crystals by the evaporation of a soln. of the component salts. A. Kurtenacker and co-workers studied the equilibrium conditions in the system: NiF_2–KF–H_2O, at 20°, and, representing the solubility *S* grms. of salt per 100 grms. of soln., found:

KF	1·21	3·52	6·32	9·64	12·9	16·8
NiF_2	1·98	1·20	0·80	0·52	0·40	0·01

and similarly at 50°. R. Wagner also prepared **sodium nickel trifluoride,** $NaF.NiF_2.H_2O$, in a similar manner. The composition of these trifluorides is not well established.

P. C. Ray and P. B. Sarkar prepared **beryllium nickel fluoride,** or **nickel fluoberyllate,** $NiBeF_4.7H_2O$, analogous with $NiSO_4.7H_2O$. N. N. Ray also prepared this salt by the action of nickel nitrate on the theoretical quantity of ammonium fluoberyllate. J. J. Berzelius evaporated a mixed soln. of nickel and aluminium fluorides and obtained long, pale, apple-green crystals slowly soluble in water; and R. F. Weinland and O. Köppen obtained **aluminium nickel pentafluoride,** $AlF_3.NiF_2.7H_2O$, by evaporating a soln. of aluminium hydroxide and nickel hydroxide or carbonate in dil. hydrofluoric acid, at ordinary temp., over lime. The small, green crystals are sparingly soluble in hydrofluoric acid. E. Rimbach and H. F. C. Kilian obtained apple-green crystals of **ceric nickelous decafluoride,** $2CeF_4.NiF_2.7H_2O$, by mixing soln. of ceric and nickelous hydroxides in hydrofluoric acid. R. Weber prepared green crystals of **titanium nickel hexafluoride,** $NiTiF_6.6H_2O$, from soln. of titanium dioxide and nickel oxide in hydrofluoric acid. The salt is soluble in water. For the corresponding salt with silicon, *vide* the fluosilicates, **6.** 40, 56. J. C. G. de Marignac prepared **zirconium nickel octofluoride,** $2NiF_2.ZrF_4.12H_2O$, soluble in water; **zirconium nickel hexafluoride,** $NiZrF_6.6H_2O$, soluble in water; **potassium zirconium nickel dodecafluoride,** $K_2Ni.ZrF_6.8H_2O$, soluble in water; and **stannic nickel hexafluoride,** $NiSnF_6.6H_2O$, soluble in water; the trigonal crystals have the axial ratios, $a:c=1:0·5145$ and $\alpha=112°\ 14'$.

A. Streng prepared **columbium nickel fluoride,** $Ni_3H_4Cb_2F_{20}.19H_2O$. E. Petersen obtained **vanadium nickel pentafluoride,** $NiVF_5.7H_2O$, by evaporating hydrofluoric acid soln. of vanadium trifluoride and nickel carbonate. The crystals are probably monoclinic with the prism angle 57° 45′. They are isomorphous with the corresponding cobalt salt; and they lose water when heated to 200° but not at 100°. A. Piccini and G. Georgis prepared **vandyl nickel tetrafluoride,** $VOF_2.NiF_2.7H_2O$, by dissolving vanadic acid, and rather less than the required mol. proportion of nickel carbonate in hydrofluoric acid. When the soln. is intensely blue, it is filtered and evaporated. The green crystals are isomorphous with those of the cobalt salt. E. Petersen prepared emerald-green crystals of **chromic nickelous pentafluoride,** $CrNiF_5.7H_2O$, by evaporating a mixed soln. of

chromic fluoride and nickel carbonate in hydrofluoric acid. The crystals are probably monoclinic, with the prism angle $\alpha=57° 25'$. They are isomorphous with the corresponding cobalt salt. The crystals are stable at 100°, but give off water at 200°. M. Delafontaine prepared **tungsten or molybdenum nickel dioxytetrafluoride,** $NiF_2.MoO_2F_2.6H_2O$, by evaporating a hydrofluoric acid soln. of nickel and tungsten or molybdenum oxides. J. C. G. de Marignac obtained a **tungsten nickel dioxytetrafluoride,** $NiF_2.WO_2F_2.10H_2O$, in deliquescent crystals. O. T. Christensen prepared **manganic nickel pentafluoride,** $MnF_3.NiF_2.4H_2O$, soluble in water; and R. F. Weinland and O. Köppen, **nickelous ferric fluoride,** $Ni[FeF_5].7H_2O$.

Nickelic fluoride.—G. A. Barbieri and J. Calzolari were unable to prepare nickelic fluoride, NiF_3, corresponding with cobaltic fluoride, CoF_3, and ferric fluoride, FeF_3, by the electrolysis of soln. of nickelous fluoride in fuming hydrofluoric acid.

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§ 14. Nickel Chlorides

The ferrous chloride found in meteorites has been called lawrencite—*vide* **13**. 66, 36. In 1838, C. T. Jackson[1] observed that the meteorite of Lime Creek, Alabama, contained both nickelous and ferrous chlorides; and W. Wicke and F. Wöhler observed nickel chloride in the form of dark green stagmatites in a meteorite from Obernkirchen; and A. Ben-Saude, in a meteorite from San Julias, near Ponte de Lime. The subject was discussed by E. Cohen.

H. Rose[2] prepared anhydrous **nickel chloride,** $NiCl_2$, by heating finely-divided nickel to low redness in a current of chlorine—the metal burns with a vivid glow, and forms yellow, crystalline scales resembling mosaic gold. H. Davy said that the metal requires heating for it to burn in chlorine. L. R. von Fellenberg, and H. Rose obtained it by decomposing heated nickel sulphide with chlorine

when a sublimate of nickel chloride and sulphur chloride is formed. J. L. Proust evaporated a soln. of nickel chloride and dehydrated the residue by heat; O. L. Erdmann added that the product can be sublimed in a retort. The spangles of nickel chloride fly about in the retort as they rise. A small proportion of the chloride is decomposed by the oxygen of the air, and chlorine is set free so that if the operation is not continued long enough for all the chloride to sublime, some remains at the bottom of the retort as a mass resembling mosaic gold, and grey nodules of nickel oxide appear on the sides of the retort. Hence, T. W. Richards and A. S. Cushman, and D. I. Ryabchikoff and V. M. Shulman, recommended dehydrating the hydrated chloride at 140°, and then subliming it in a current of hydrogen chloride, and A. L. Potilitzin recommended heating commercial nickel chloride in chlorine. H. Quantin obtained the chloride by heating nickel oxide in a current of carbon tetrachloride; C. Poulenc, by heating nickel fluoride in a current of hydrogen chloride; and S. P. L. Sörensen, by heating nickel hexamminochloride to drive off the ammonia.

J. L. Lassaigne thought that the anhydrous chloride contained more chlorine than corresponded with $NiCl_2$, and C. F. Bucholz, less chlorine; but the composition of the anhydrous chloride was established by the analyses of O. L. Erdmann, L. R. von Fellenberg, and P. Berthier—*vide supra*, the at. wt. of nickel. The hydrates of nickel chloride have not been thoroughly investigated. O. Lehmann said that the tendency to form large crystals is greater, the larger is the degree of hydration. R. Tupputi observed that the soln. of nickel in aqua regia, or of nickel oxide, hydroxide or carbonate in hydrochloric acid, when evaporated and cooled, furnishes grass-green crystals. According to O. L. Erdmann, when the soln. is evaporated to dryness, the brownish-yellow mass, on exposure to air, acquires, first a lemon-yellow and then a green colour, and it dissolves in water with a large rise of temp. If the evaporation has been carried too far, flakes of nickel oxide remain undissolved. The sublimed chloride was found by J. L. Proust, and H. Rose to become pale green after a few days' exposure to air, and the salt is then freely soluble in water; L. R. von Fellenberg said that if the chloride be not first exposed to air, it dissolves in water very slowly, and, added J. L. Proust, only when boiled in water for a long time—even hot hydrochloric acid dissolves it with difficulty. P. Sabatier, G. P. Drossbach, and A. C. Becquerel found that the crystals which separate at ordinary temp. are those of the *hexahydrate*, $NiCl_2.6H_2O$; this agrees with the analyses of A. Laurent, and J. C. G. de Marignac. P. Sabatier observed that if the hexahydrate be allowed to stand in vacuo over conc. sulphuric acid, at a summer's temp., for 3 months, it forms the *dihydrate*, $NiCl_2.2H_2O$. A. Johnsen obtained the dihydrate by heating the hexahydrate for an hour at 30°. For H. W. Foote's observations on the dihydrate, and the *tetrahydrate*, $NiCl_2.4H_2O$; and those of I. H. Derby and V. Yngve on the tetrahydrate, *vide infra*. A. Ditte reported that if a soln. of hexahydrate be saturated with hydrochloric acid, there separates out, at 12°, a yellowish-green powder of the *monohydrate*, $NiCl_2.H_2O$. The report of the monohydrate has not been confirmed. P. A. Favre and C. A. Valson discussed the properties of what they regarded as a *heptahydrate*, but this was probably the hexahydrate; and F. Rüdorff, the *dodecahydrate*, which was probably a cryohydrate, not necessarily the eutectic.

The physical properties of nickel chloride.—Sublimed nickel chloride furnishes crystalline scales which feel like mica; and which appear pale yellow when separate, and golden yellow in mass; when produced by the dehydration of the hydrate, the salt furnishes a brownish-yellow, earthy mass. According to A. Ferrari, the X-radiograms of the **crystals** correspond with a rhombohedral-pseudo-cubic-lattice of the magnesium or cadmium chloride type, having $a=7{\cdot}07$ A., $c=17{\cdot}32$ A., and $a:c=1:2{\cdot}45$, with 16 molecules per cubic lattice. G. Bruni and A. Ferrari, and V. M. Goldschmidt and co-workers studied the subject. L. Pauling gave $a=6{\cdot}13$ A., and added that each nickel atom is probably surrounded by six chlorine atoms approximately at the corners of a regular octahedron, six edges of

which are shared with other octahedra so as to form a layer. The cadmium chloride structure seems to be the stable one for substances of the type MX_2, where M has the co-ordination number 6, and the anion has a small polarizability. The monohydrate furnishes a yellowish-green, crystalline powder; the dihydrate is straw-yellow; the tetrahydrate, according to A. Neuhaus, is a pale yellowish-green; and the hexahydrate forms green or grass-green monoclinic prisms which are isomorphous with the crystals of the corresponding hexahydrated cobalt chloride. According to J. C. G. de Marignac, the axial ratios of the crystals of the hexahydrated chloride are $a:b:c=1{\cdot}4678:1:0{\cdot}9426$, and $\beta=122°\ 30'$. Twinning occurs about the (110)-plane. The (001)-cleavage is perfect. The double refraction is strong and positive. O. Mügge gave for the axial ratios of the hexahydrate $a:b:c=1{\cdot}4792:1:0{\cdot}9468$, and $\beta=87°\ 58'$, and he added that the crystals are not isomorphous with bischofite, $MgCl_2.6H_2O$, since they are deformed along different gliding planes. S. Makishima studied the lattice energy; and M. Yamada, the influence of a magnetic field on the crystal form.

H. Schiff gave 2·56 for the **specific gravity** of the anhydrous salt; W. Biltz and E. Birk, 3·521 for the sublimed, and 3·508 for the synthetic salt at 25·14°; G. P. Baxter and F. A. Hilton, 3·54; and A. Ferrari calculated 3·45 from observations on the X-radiograms. J. H. Long gave 50·7 for the mol. vol. of the salt. P. A. Favre and C. A. Valson obtained 1·921 for the sp. gr. of the hexa- (or hepta-) hydrate; and A. Neuhaus gave 1·84 for the sp. gr. of the hexahydrate; 2·217 for the tetrahydrate; and 2·4 for the dihydrate. Observations on the sp. gr. of aq. soln. were made by A. C. Becquerel, W. Biltz, L. Brant, G. Dreyer, B. Franz, G. T. Gerlach, J. A. Groshans, A. Heydweiler, H. C. Jones and co-workers, S. Lussana and G. Bozzola, L. Mond and R. Nasini, P. Moretto, and G. Quincke. The general results correspond with:

$NiCl_2$.	1	4	8	12	16	20	25	30 per cent.
Sp gr. .	1·0078	1·0370	1·0777	1·1209	1·1655	1·2150	1·2800	1·3535

R. Wagner gave for N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-$NiCl_2$, the respective values 1·0591, 1·0308, 1·0144, and 1·0067 at 25°. P. Moretto, A. Taffel, and S. Lussana and G. Bozzola discussed the temp. of **maximum density**; and G. Dreyer gave for soln. with 0·508, 1·033, and 2·104 per cent. of $NiCl_2$, the lowerings of the temp. of maximum density of water, 3·96°, respectively, 0·64°, 1·31°, and 2·104°. P. A. Favre and C. A. Valson found with N-gram-equivalents of nickel chloride per kgrm. of water, the following values for the sp. gr. of the soln. at 23·1°; for the vol. obtained by dividing the total weight of water and salt by the sp. gr.; and for the successive increments in vol. produced by adding another eq. of the salt:

N-gram-eq. . . .	1	2	3	4	5	6
Sp. gr. . . .	1·061	1·119	1·176	1·230	1·284	1·335
Total volume . .	1004	1009	1016	1024	1032	1041 c.c.
Increments in vol. .	4	5	7	8	8	9 c.c.

and they also obtained results for soln. of the hexahydrate. W. W. J. Nicol, F. Ephraim, and W. Fischer measured the **molecular volume** of the salt. J. H. Long studied the **diffusion** of the salt in aq. soln., and F. Voigtländer gave for soln. with 7·2 mgrms. of salt per c.c., the diffusion coeff. in agar-agar, 0·454, 0·840, and 1·480 sq. cm. per day, respectively, at 0°, 20°, and 40°. R. Wagner gave for the **viscosity** of N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln., at 25°, respectively, 1·2055, 1·0968, 1·10443, and 1·0210—water unity. G. Tammann studied the **inner pressure** of soln.

J. C. G. de Marignac found the **specific heat** of aq. soln. of nickel chloride, between 24° and 55°, with 25 and 200 mols of water per mol of salt, to be, respectively, 0·7351 and 0·9451. The subject was studied by N. de Kolossowsky, and K. Jauch. According to O. L. Erdmann, nickel chloride may be repeatedly sublimed without fusing; the sublimation in vacuo takes place without decom-

position, but in air, a little chlorine is set free, and a little nickel oxide is formed. C. G. Maier obtained for the **vapour pressure,** p mm., of the anhydrous salt:

	541·0°	759·7°	826·5°	872·1°	901·6°	927·5°	945·2°	972·7°	994·0°
p .	38·9	55·9	87·9	139·6	222·8	338·1	481·6	617·3	820·6

R. Uloth, and K. Jellinek and R. Uloth studied the subject. H. Lescœur found the **dissociation pressure** of the hexahydrate, at 20°, to be 4·6 mm. G. Tammann gave for the lowering of the vap. press. of water at 100°, by the dissolution of 6·45, 28·23, 46·83, and 63·74 grms. of salt per 100 grms. of water, respectively, 16·1, 95·0, 185·3, and 270·1 mm. I. H. Derby and V. Yngve, and C. Dieterici measured the vap. press. of hydrated nickel chloride, and of its sat. soln., and the results show that for soln. of concentration C, the vap. press., p mm. at θ, are:

C .	64·0			69·5		73·6			
θ .	19·8°	24·1°	30·3°	35·1°	36·25°	40·57°	45·22°	48·34°	54·10°
p .	9·6	12·0	17·0	21·5	22·5	28·9	36·7	42·6	56·4 mm.
Solid phase	$NiCl_2.6H_2O$					$NiCl_2.4H_2O$			

The results for sat. soln., and for hydrates in the presence of the vapour, are summarized in Fig. 323. The **transition temperature** for $NiCl_2.6H_2O \rightleftharpoons NiCl_2.4H_2O + 2H_2O$ is 36·25°; and for $NiCl_2.4H_2O \rightleftharpoons NiCl_2.2H_2O + 2H_2O$, is near 75°. The solubility data give, respectively, 29° and 64°—*vide infra.*

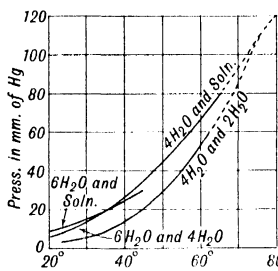

FIG. 323.—Vapour Pressures of Hydrates and Saturated Solutions of Nickel Chloride.

W. Biltz gave for the lowering of the f.p., $\theta°$, of aq. soln. with 0·2825, 0·8269, 2·214, and 5·058 grms. of $NiCl_2$ per 100 grms. of water, respectively, θ=0·110°, 0·312°, 0·839°, and 2·030°. H. C. Jones and co-workers observed a minimum in the curve for the mol. **lowering of the freezing point** in the vicinity of 0·5N-soln. Observations were also made by N. Tarugi and G. Bombardini, and R. Salvadori. The last-named also gave for the **raising of the boiling point** of soln. with 2·86, 6·14, and 9·18 grms. of $NiCl_2$ in 100 grms. of water, respectively, 0·30°, 0·67°, and 1·17°. Observations were also made by N. Tarugi and G. Bombardini. E. Beckmann found that the mol. wt. of nickel chloride in boiling quinoline is normal. W. Fischer and R. Gewehr gave 1001° for the **melting point.** C. G. Maier obtained 973·4° for the b.p. of the anhydrous salt, and for the **heat of vaporization,** 53·41 Cals. per mol. both at 973·4° and at 752·6°.

The **heat of formation** of the anhydrous chloride was found by J. Thomsen to be (Ni,Cl_2)=74·53 Cals.; $(Ni,Cl_2,Aq.)$=39·7 Cals.; $(Ni,2HCl,Aq.)$=16·19 Cals.; $(Ni,Cl_2,6H_2O)$=94·86 Cals.; and $(NiCl_2,6H_2O)$=20·33 Cals. The **heat of neutralization** of $\frac{1}{2}Ni(OH)_2$ by HCl aq. is 11·29 Cals.; and the **heat of solution** of a mol. of $NiCl_2$ in 400 mols. of water is 19·17 Cals.; and for a mol. of $NiCl_2.6H_2O$ in 400 mols. of water is —11·60 Cals. P. Sabatier gave 10·3 Cals. for the heat of soln. of the dihydrate at 19·5°. The subject was studied by E. Rabinowitsch and E. Thilo, F. Ephraim, and O. Schütz and F. Ephraim. E. Plake studied the **heats of dilution** of aq. soln. M. de K. Thompson and M. W. Sage found the **free energy** of formation of the salt from nickel and chlorine at atm. press. to be 74·4 Cals. The subject was studied by G. Beck. W. Klemm discussed the relation between the lattice energy and the heat of formation.

L. Mond and R. Nasini found the **refractive index** of a soln. of nickel chloride of sp. gr. 1·10251 to be 1·35593 for the H_α-line, 1·35793 for the D-line, and 1·36276 for the H_β-line. This gives for the sp. and mol. refractions by the μ-formula, respectively, 0·2256 and 29·24; and by the μ^2-formula, respectively, 0·1209 and

16·06. H. C. Jones and F. H. Getman found the refractive indices, μ, of soln. with M mols per litre to be :

M .	0·037	0·074	0·149	0·223	0·372	0·446	0·521	0·743
μ .	1·32672	1·32790	1·32965	1·33240	1·33684	1·33894	1·34106	1·34710

H. M. Vernon discussed the changes of colour which occur on dilution, and on raising the temp. of aq. soln. The **absorption spectrum** of aq. soln. was studied by G. Denigès, S. M. Karim and R. Samuel, H. Fesefeldt, J. Angerstein, T. Dreisch, W. N. Hartley, M. Pavlik, S. Datta and M. Deb, J. Gielessen, Y. Shibata and K. Harai, and Y. Shibata—*vide supra*, the spectral properties of nickel; and the ultra-violet absorption spectrum of soln., by J. von Koczkas. P. Mesnage observed bands in the **arc spectrum** of nickel chloride which he attributed to **nickel subchloride**, NiCl. The **X-ray absorption spectrum** was studied by S. Aoyama and co-workers, W. V. Bhagwat, K. Fajans, and O. Stelling; and the anomalous **dispersion,** by R. W. Roberts. H. Ollivier and co-workers found that the **magnetic rotation** of nickel chloride in aq. soln. decreases slightly with a fall of temp., but increases in methyl alcohol soln. F. Allison and E. J. Murphy also studied the magneto-optical properties; J. Cichocky, the **emission of positive ions** by the salt; T. Peczalsky and J. Cichocky, thermionic emission; P. Krishnamurti, the **Raman effect;** R. W. Roberts and co-workers, the magnetic rotatory power; E. F. Rousseau, the fixation of energy by exposure to sunlight; and C. J. Gorter obtained a negative result in attempting to increase the frequency of radiations by impinging light on a soln. of nickel chloride.

W. Hampe observed that fused nickel chloride is a good electrical conductor. G. Vicentini, and L. de Brouckère made some observations on the electrical conductivity of aq. soln., and E. Franke found the eq. conductivity, λ, of soln. with a gram-equivalent of the salt, in v litres of water at 25°, to be :

v	32	64	128	256	512	1024
λ	107·2	113·9	118·3	122·6	125·6	127·1

and W. Althammer gave, at 25° :

v	20	40	80	320	1280	5120
λ	96·5	101·7	107·8	115·8	121·5	125·2

Observations were also made by H. C. Jones and co-workers, and N. Tarugi and G. Bombardini. H. F. Haworth studied the conductivity with alternating currents. W. H. Banks and co-workers discussed the **ionization** of the salt in aq. soln. H. G. Denham measured the e.m.f. of the cell $H_2 \mid NiCl_2,NH_4NO_3 \mid Hg_2Cl_2$-electrode, for soln. with a mol. of nickel chloride in v litres, and found for the **H'-ion concentration,** and the **degree of hydrolysis :**

v	4·4	8·8	17·6	35·2
Electromotive force . .	0·04927	0·5032	0·5109	0·5229 volt
H'-ion concentration $\times 10^3$	0·290	0·184	0·132	0·086
Percentage hydrolysis .	0·127	0·160	0·230	0·300
$K \times 10^5$	0·36	0·29	0·27	0·36

If x denotes the fractional degree of hydrolysis, then $K = x_2/(1-x)v$, on the assumption that there is a first stage hydrolysis $NiCl^{\cdot} + OH' \rightleftharpoons NiCl(OH)$. The average value for K is $0·30 \times 10^{-5}$. C. Kullgren observed

	85·5°			100°		
v . . .	4	16	64	4	16	64
Hydrolysis .	0·0084	0·0084	0·0084	0·0131	0·0142	0·0194 per cent.

and for a 0·5N-soln. at 55·5°, 0·048 per cent. W. Althammer estimated for 0·05M- and 0·01M-$NiCl_2$, the respective percentage hydrolysis 0·14 and 0·16. T. Katsurai, H. W. Vernon, and A. Günther-Schulze studied the subject. H. C. Jones and co-workers calculated the **degree of solvation** of the salt, *i.e.*, the degree of hydra-

tion expressed as the number of mols. of water in combination with a mol. of the salt at the given concentration, M mols per litre, when a litre of the soln., at the concentration, contained 1000 grms. of water. They found :

M	0·074	0·297	0·521	0·900	2·000	3·483
Solvation	36·9	31·7	27·4	25·7	19·0	13·8

O. Hassel, and M. Pavlik studied the subject. M. Martin and M. Delamotte, E. and A. C. Becquerel, T. Fearn, and G. Gore studied the **electrodeposition** of nickel from soln. of the chloride—*vide supra.* H. V. Tartar and H. K. McClain studied the **electromotive force** of $0{\cdot}056M$-$NiCl_2$ between platinum electrodes ; G. Tammann and H. O. von Samson-Himmelsjerna, between nickel chloride ; and H. G. Denham, that of the cell indicated above. A. H. W. Aten and co-workers studied the deposition of nickel from the fused chloride—*vide supra ;* J. M. Merrick, the **electrolysis** of aq. soln. ; C. Charmetant, the electrolysis of nickel chloride in aqueous and alcoholic solutions ; W. Pavlik, and F. Förster and K. Georgi, the **deposition potential ;** K. Hess and K. Jellinek, the **activity coefficient ;** and C. Schall, the **anodic oxidation** of the salt in HCl-alcoholic soln. where there is evidence of the formation of **nickel trichloride,** $NiCl_3$. H. J. Blikslager obtained evidence of the formation of complex ions $NiCl_3{}'$ and of $NiCl_4{}''$ in the electrolysis of soln. of nickel chloride in fused alkali chloride at 470° and 720°. E. Bouty measured the **thermoelectric force** of aq. soln. of the salt.

P. Théodorides gave for the magnetic susceptibility of the solid chloride, $45{\cdot}57\times10^{-6}$ mass unit ; and T. Ishiwara, $44{\cdot}7\times10^{-6}$. W. Klemm and W. Schüth gave for $\chi\times10^6=89{\cdot}3$, 48·2, 24·5, and 16·8, respectively, at −78°, 20°, 220°, and 400° ; and K. Honda and T. Ishiwara :

	−76·3°	−16·4°	18·1°	115·1°	254·6°	511·0°	758·4°	846·7°
$\chi\times10^6$	85·1	55·6	46·7	31·4	22·0	14·3	11·0	10·0

O. Liebknecht and A. P. Wills gave for aq. soln. at 18°, 35×10^{-6} mass unit ; G. Quincke, 44×10^{-6} ; G. Jäger and S. Meyer, 40×10^{-6} ; and G. Falckenberg, $34{\cdot}8\times10^{-6}$. Observations on the magnetic properties were made by L. S. Brant, S. Datta, L. Landau, D. M. Bose and P. K. Raha, A. Serres, B. Cabrera and co-workers, G. Foëx and B. Kessler, W. Klemm and W. Schüth, G. Falckenberg, H. Fahlenbrach, S. S. Shaffer and N. W. Taylor, A. Serres, W. Pavlik, P. Weiss and E. D. Bruins, L. A. Welo, and H. R. Woltjer and H. K. Onnes, H. Fahlenbrach studied the magnetic moment ; and G. Roasio, the effect of a magnetic field on the crystallization of nickel salts. M. Yamada observed that when a crystal of nickel chloride in a soln. of the same salt is placed in a strong magnetic field, slightly inclined faces appear on the crystal.

The chemical properties of nickel chloride.—A. Hantzsch and H. Carlsohn discussed the nature of this salt. H. Rose observed that nickel chloride is easily reduced to the metal when it is heated in **hydrogen**. P. Schützenberger thought that a volatile compound, perhaps NiHCl, is formed, but this has not been confirmed. G. Crut observed that the reduction involves a reversible reaction so that equilibrium is attained at 445° when the concentration of the hydrogen chloride is about 59 per cent. The equilibrium constant, $K=Q/4571T+\log p+\log[HCl]^2/[H_2]$, where p is the equilibrium press., and Q the heat of the reaction, −30·7 cals. at 15°. $K=11{\cdot}28$ between 310° and 415°. Equilibrium is attained at 430° in about 12·5 minutes from the hydrogen-nickel chloride end, and in about 11 hrs. from the other end. This is attributed to a retardation produced by nascent hydrogen clinging to the surface of the metal. R. Uloth, J. H. Weibel, K. Jellinek and co-workers studied the reaction. E. Berger and G. Crut discussed the reaction. S. Miyamoto noted the reduction of the chloride by hydrogen in the silent discharge. W. N. Ipatéeff observed that $0{\cdot}2N$-$NiCl_2$ deposits a little nickel under the influence of hydrogen at 100 atm. press., and 250°. O. L. Erdmann found that when the chloride is heated in **air,** green,

pulverulent nickel oxide, more or less free from chloride, can be obtained; and H. Schulze said that the oxidation is complete. H. W. Hake studied the deliquescence of the salt in air. H. Baubigny observed that with moist **oxygen,** at 350° to 440°, the transformation is complete. K. Jellinek and A. Rudat studied the action of oxygen on nickel chloride between 300° and 600°, and found that nickelous oxide alone is formed. A. Mailfert observed that the salt is slowly attacked by **ozone.** Anhydrous nickel chloride becomes pale green on exposure to air, owing to the absorption of moisture. The crystals of the hexahydrate can be preserved indefinitely when kept in a sealed tube. R. Tupputi found that the green crystals of the hexahydrate either deliquesce or effloresce in air according to the degree of humidity. H. W. Hake said that the maximum hydration attained corresponds with $NiCl_2.17H_2O$. The subject was studied by M. A. Rakuzin. The dissolution of the sublimed chloride in water is slow unless the salt has been previously allowed to deliquesce in air. R. Tupputi said that the hexahydrate is freely soluble in one to one and a half times its weight of cold water. A. Étard gave for the percentage solubility of the hexahydrate, *S* grms. of anhydrous salt, and starting with the hexahydrate as solid phase:

	−17°	−16°	10°	18°	38°	59°	78°	96°
S . .	29·7	31·0	37·3	38·5	41·9	45·0	46·6	46·7 per cent.

H. Benrath gave for the percentage solubility, *S*,

	0°	17·5°	25°	40·5°	50°	60°	75°	99·5°
S . .	34·8	37·07	39·58	42·20	43·17	44·84	46·32	46·71 per cent.
	$NiCl_2.6H_2O$			$NiCl_2.4H_2O$			$NiCl_2.2H_2O$	

The transition temp. are 29° for the hexahydrate to the tetrahydrate, and 64° for the tetrahydrate to the dihydrate; but the vap. press. data give respectively 36·25°, and 75°—*vide supra.* The data of H. Benrath, and E. Boye are plotted in Fig. 324. P. Kuznetzoff studied the hydrates of nickel chloride; and T. Reiff, the tendency of the hydrates to form aquo-salts. Solubility observations were also made by C. F. Kullgren, and H. G. Denham. H. W. Foote obtained 35·27 per cent. for the solubility of the hexahydrate at 0°; A. Ditte said that a litre of water dissolves 600 grms. of the hexahydrate; and Y. Osaka and T. Yaginuma, that water dissolves 38·88 per cent. of $NiCl_2$ at 25°. R. Reinicke studied the nature of the hydrates. The eutectic temp. and the ice-line of the solubility curve were studied by F. Rüdorff, and F. Guthrie —*vide supra.* Basic salts have been reported. The hydrolysis of the salt has been discussed previously. J. J. Berzelius thought that a **nickel oxychloride** is formed. H. W. Fischer observed that when the aq. soln. is heated in an autoclave, a pale green, amorphous precipitate is formed. G. André reported a pale green precipitate to be formed when aq. ammonia is gradually added to a soln. of nickel chloride, but in an amount not sufficient for the complete precipitation of the nickel. The composition was $8NiO.NiCl_2.13H_2O$. There is nothing here to establish the chemical individuality of a basic chloride. F. Reiff discussed the complex $[NiCl_2(OH)(H_2O)]H.C_4H_8O_2$. W. Feitknecht said that the lattice of $NiCl_2.4Ni(OH)_2$ corresponds with alternate layers of the normal salt and of hydroxide. H. G. Denham thought that **nickel hydroxychloride,** Ni(OH)Cl, is formed by the hydrolysis of the salt—*vide supra.* E. Hayek studied the basic chlorides. G. Pellini and D. Meneghini examined the action of **hydrogen dioxide** in alkaline soln.—*vide supra,* nickel dioxide. R. Kunn and A. Wassermann studied the action of nickel salts on hydrogen dioxide.

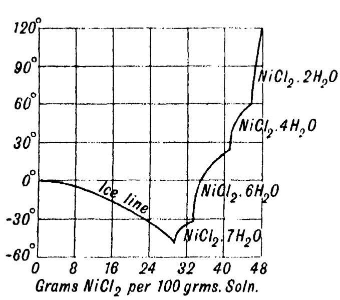

FIG. 324.—The Solubility Curve of Nickel Chloride.

K. Fredenhagen and G. Cadenbach observed that the chloride does not dissolve in **hydrofluoric acid.** R. F. Weinland and F. Schlegelmilch prepared a complex with **iodine trichloride,** namely, **nickel diiodohexachloride,** $NiCl_2.2ICl_3.8H_2O$. K. Fredenhagen observed that nickel chloride is not affected by **hydrofluoric acid.** O. Löw, and M. G. Levi and V. Bettoni observed that when nickel chloride is heated in a current of air and **hydrogen chloride,** chlorine is evolved so that the nickel salt acts like the copper salt employed in Deacon's process for chlorine. A. G. Page discussed nickel chloride as a chlorinating catalyst. R. J. Kane noted that a mol. of nickel chloride absorbs a mol. of hydrogen chloride, and gives it up on exposure to air. According to A. Ditte, the solubility of nickel chloride in water decreases steadily in the presence of increasing proportions of **hydrochloric acid,** and more so with hot than with cold soln. Whilst a sat. soln. of nickel chloride containing 600 grms. of salt per litre deposits green crystals of the hexahydrate when cooled, only 40 grms. of the salt dissolves in a litre saturated with hydrogen chloride at 18°, and the liquid deposits yellowish-green crystals of the monohydrate (probably dihydrate) when cooled. The three component system was investigated by H. W. Foote. Expressing concentrations in grams per 100 grms. of sat. soln., at 0°, he found:

$NiCl_2$.	35·27	26·71	6·15	4·56	4·45	1·40	0·82	0·43
HCl .	0·00	6·53	21·70	26·00	26·23	35·03	37·22	40·61
Solid phase		$NiCl_2.6H_2O$			$NiCl_2.4H_2O$		$NiCl_2.2H_2O$	

The results are plotted as a portion of a ternary diagram, Fig. 325. Observations were made by A. V. Babaeva and T. A. Artschakova. N. A. Isgarischeff and S. Schapiro observed the accelerating action of nickel chloride in the attack of marble by hydrochloric acid. F. Reitzenstein dissolved nickel oxide in rather more pyridine than is required for preparing a tripyridine-derivative, diluted the soln. with absolute alcohol, added a little dil. hydrochloric acid, saturated the liquid with dry hydrogen chloride, decanted off the clear liquor, and allowed it to stand when, very soon, a yellowish-green **nickel hydrochloride,** $3NiCl_2.2HCl.1\frac{1}{2}H_2O$, separated out. It can be freed from pyridine by washing with alcohol and ether. A. J. Balard observed that when the aq. soln. of nickel chloride is treated with **hypochlorous acid,** chlorine is evolved, and nickel hydroxide is precipitated.

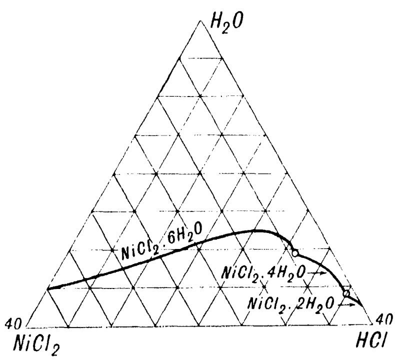

FIG. 325.—Ternary System: $NiCl_2$–HCl–H_2O at 0°.

H. Baubigny observed that **hydrogen sulphide** does not react with a soln. of nickel chloride so readily as it does with the sulphate. J. Myers, and O. Löw found that when nickel chloride is heated with potassium sulphide, nickel, and alkali polysulphide are formed, and H. de Sénarmont noted that in a sealed tube at 160°, nickel sulphide is produced. H. L. Haken studied the action of **hyposulphites** on soln. of nickel salts; and A. Hantzsch and H. Carlsohn, the action of dil. **sulphuric acid.** O. Hassel and H. Kringstad observed that the compound formed with **fluosulphonic acid,** namely, **nickel hexamminofluosulphonate,** $[Ni(NH_3)_6](SO_3F)_2$, has a lattice with a=11·47 A.

T. W. B. Welsh and H. J. Broderson observed that 100 c.c. of anhydrous **hydrazine** dissolve 8 grms. of nickel chloride at room temp., forming a blue soln. C. Paal and L. Friederici added that no reduction occurs at 100°. H. Franzen and O. von Mayer prepared **nickel dihydrazinochloride,** $NiCl_2.2N_2H_4$, by mixing a hot, aq. soln. of 25 grms. of nickel chloride in 100 c.c. of water, with 40 c.c. of 50 per cent. hydrazine hydrate. The washed precipitate, dried over potassium

hydroxide and conc. sulphuric acid, is bluish-white, and it is freely soluble in aq. ammonia and in dil. acids. Y. Shibata studied the absorption spectrum; and S. Datta, the magnetic properties. According to H. Franzen and O. von Mayer, if 12 grms. of nickel hexamminochloride are treated with 40 c.c. of a 50 per cent. soln. of hydrazine hydrate, and the blue soln. is warmed on a water-bath, ammonia is evolved, and a violet-red, crystalline powder of **nickel trihydrazinochloride,** $NiCl_2.3N_2H_4$, is formed. It is freely soluble in dil. acids, forming a green liquid. Y. Shibata studied the absorption spectrum.

G. Gore, and E. C. Franklin and C. A. Kraus noted that nickel chloride is insoluble in liquid **ammonia**; T. Vorster, that the chloride is reduced to metal when it is heated in dry ammonia; and O. L. Erdmann, that aq. ammonia slowly dissolves the chloride, forming a blue soln.—even in the absence of air. M. Berthon, and J. Persoz discussed the ammines of the nickel salts. H. Rose observed that anhydrous nickel chloride, at ordinary temp., absorbs ammonia gas, and the reaction is attended by tumefaction and the evolution of heat, until **nickel hexamminochloride,** $NiCl_2.6NH_3$, is formed. O. L. Erdmann obtained a similar product by adding alcohol to a soln. of nickel chloride in aq. ammonia; and H. Rose, by crystallization from a soln. of the chloride in an excess of ammonia. H. A. Frasch treated an aq. soln. of nickel chloride, sulphate, or nitrate with an excess of ammonia, and added alkali chloride. The precipitate which was formed was washed with an ammoniacal soln. of alkali chloride. He also obtained it by the action of ammonia on nickel carbonate in the presence of alkali chlorides. S. P. L. Sörensen treated a soln. of nickel nitrate with aq. ammonia until the precipitate first formed re-dissolved. He then added an ammoniacal soln. of ammonium chloride to the filtered liquid, as long as a precipitate was formed. The precipitate was washed with an ammoniacal soln. of ammonium chloride, then with conc. aq. ammonia, then with a mixture of conc. aq. ammonia and alcohol, and finally with alcohol. H. Rose described the hexammine as a white powder with a tinge of blue; O. L. Erdmann, as a blue powder, or as large, opaque octahedra with truncated edges and summits, and blue with a violet iridescence; and H. A. Frasch, as large, violet-blue, pyramidal crystals. The subject was studied by G. L. Clark, E. Kocsis, and H. J. de Wijs. P. Stoll found that the X-radiograms corresponded with a face-centred, cubic lattice of the calcium fluoride type. There are 4 mols. in the elementary cell; and the lattice parameter is $a=10{\cdot}15$ A. The nickel atoms are located at the corners and centres of the faces of the cube. Each nickel atom is surrounded by six NH_3-groups arranged at the corners of an octahedron, and the chlorine atoms are arranged at the corners of a cube—*vide* Figs. 115 to 117, **14.** 67, 21, for the corresponding cobaltammine. R. W. G. Wyckoff gave $a=10{\cdot}09$ A. for the side of unit cell; and P. Scherrer and P. Stoll, and P. Stoll gave $a=10{\cdot}15$ A. The structure of the lattice was also studied by G. B. Naess and O. Hassel, who gave $a=10{\cdot}066$ A.; and W. Biltz, and W. Biltz and E. Birk, who gave $a=10{\cdot}14$ A. For the distance between Ni and Cl, G. B. Naess and O. Hassel gave 4·36 A., and they studied the sphere of action of the anion. W. Biltz and E. Birk gave 1·468 for the sp. gr. at 25°/4°, and 157·9 for the mol. vol. The crystals were found by F. Rose, and H. A. Frasch to be stable when kept in a closed vessel, but they deliquesce in air, and in dry air, they lose ammonia; and O. L. Erdmann said that the crystals lose ammonia in warm air, or when dried in vacuo over sulphuric acid. W. Biltz and B. Fetkenheuer found the decomposition curves of the hexammine and its decomposition products represented in Figs. 326 and 327. The results show the existence, under these conditions, of the hexammine—bluish-violet, of the diammine—pale yellow, and of the monammine—yellowish-brown. The dissociation press., p mm., of the hexammine was measured by F. Ephraim, and by W. Biltz and B. Fetkenheuer. F. Ephraim's data, Fig. 327, are:

	112°	128°	144·5°	155°	164°	172·5°	177°
p . .	42	91	218	348	485	660	775

W. Biltz and B. Fetkenheuer gave 760 mm. at 176·5°, and the corresponding heat of formation is 16 Cals. per NH_3-mol. W. Biltz and G. F. Hüttig gave 14·15 Cals. per NH_3-mol.; and G. Beck gave $(NiCl_2,6NH_3)$=373 Cals. F. Ephraim and coworkers discussed the subject. W. Hieber and E. Levy studied the energy of formation; S. G. Mokruschin and E. I. Kriloff, the surface energy; H. Shiba and T. Inouye, and Y. Shibata, the absorption spectrum; I. Damaschun, the Raman effect; P. J. van Rysselberghe, the transport number of the cation $Ni(NH_3)_6$; and S. S. Shaffer and N. W. Taylor, and W. Klemm and W. Schüth, the magnetic susceptibility. The hexammine dissolves without decomposition in cold water, but when the soln. is boiled, ammonia is evolved, and green flakes of nickel hydroxide are deposited. F. Ephraim and P. Mosimann, and P. Mosimann found the solubility in water to be 15·39 grms. or 0·066 mol. per litre. H. A. Frasch observed that an aq. soln. of the hexammine is decomposed by potassium hydroxide. F. Rose observed that the salt is sparingly soluble in conc. aq. ammonia; S. P. L. Sörenson, that it is almost insoluble in an ammoniacal soln. of ammonium chloride; O. L. Erdmann, that it is insoluble in alcohol; and F. Ephraim, that

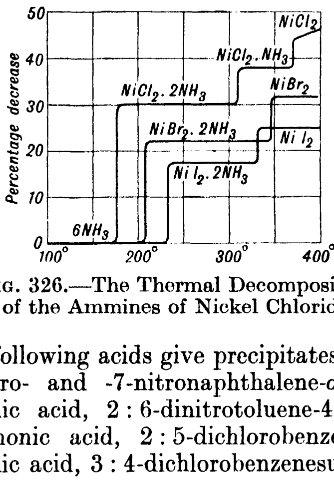

FIG. 326.—The Thermal Decomposition of the Ammines of Nickel Chloride.

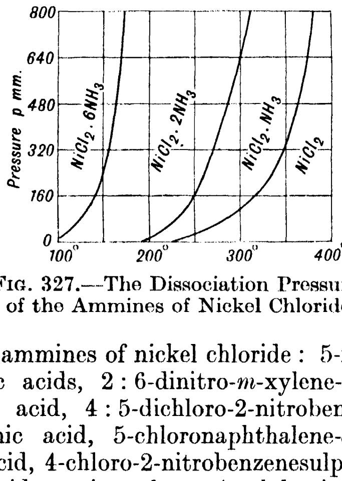

FIG. 327.—The Dissociation Pressures of the Ammines of Nickel Chloride.

the following acids give precipitates with the ammines of nickel chloride: 5-nitro-6-nitro- and -7-nitronaphthalene-α-sulphonic acids, 2 : 6-dinitro-*m*-xylene-4-sulphonic acid, 2 : 6-dinitrotoluene-4-sulphonic acid, 4 : 5-dichloro-2-nitrobenzenesulphonic acid, 2 : 5-dichlorobenzenesulphonic acid, 5-chloronaphthalene-α-sulphonic acid, 3 : 4-dichlorobenzenesulphonic acid, 4-chloro-2-nitrobenzenesulphonic acid, 2-chloro-3 : 5-dinitrobenzenesulphonic acid, *m*-nitrotoluene-4-sulphonic acid, *p*-nitrotoluene-2-sulphonic acid, dibromonaphthalene-β-sulphonic acid. L. S. Levy studied the absorption by ferric hydroxide. The di- and tri-sulphonic acids do not give precipitates with ammoniacal soln. of nickel chloride. G. André reported that a *hemihydrate*, $NiCl_2.6NH_3.\frac{1}{2}H_2O$, is formed in violet octahedra when nickel hydroxide is suspended in a well-cooled soln. of ammonium chloride, and treated with ammonia gas. G. André also said that **nickel triaquotriamminochloride,** $NiCl_2.3NH_3.3H_2O$, is formed in octahedral crystals when a warm soln. of the hexammine is cooled. Y. Shibata studied the absorption spectrum of this salt. G. B. Naess and O. Hassel obtained $[Ni(NH_3)_6](BF_4)_2$, and $[Ni(NH_3)_6](SO_3F)_2$.

F. Rose observed that **nickel diamminochloride,** $NiCl_2.2NH_3$, is formed when the hexammine is heated to 120°. O. L. Erdmann said that when the crystals are heated in vacuo, they decrepitate and crumble to a yellow powder of anhydrous nickel chloride. The dissociation press., *p* mm., of the diammine, Fig. 327, observed by F. Ephraim, are:

	215°	239°	260°	282°	296°	305°	311°
p . .	11	61·5	133	268	512·5	666	710

and at 313° the press. is 760 mm. The corresponding heat of formation is $NiCl_2.2NH_3=NiCl_2.NH_3+NH_3+21\cdot6$ Cals. W. Biltz and G. F. Hüttig gave 19·0 Cals. per NH_3-mol. for the heat of formation of the diammine. O. L. Erdmann said that at a strong red-heat, a sublimate of ammonium and nickel chlorides is

formed, and if air be present, nickel oxide remains. The diammine decomposes into yellowish-brown nickel monoamminochloride, $NiCl_2.NH_3$; and the dissociation press., p mm., Fig. 327, by F. Ephraim, are:

	265°	284·5°	311°	322°	339°	335°	373°
p . .	20	38	100	159	223	351	710

and at 375°, the press. is 760 mm. The heat of formation is $NiCl_2.NH_3 \rightleftharpoons NiCl_2 + NH_3 + 18·3$ Cals.; and W. Biltz and G. F. Hüttig gave 21·46 Cals. P. Ray and H. Bhar, and S. Datta studied the magnetic susceptibilities of **nickel dihydrazinodichloride,** $NiCl_2.2N_2H_4$; and of **nickel trihydrazinodichloride,** $NiCl_2.3N_2H_4$.

E. Divers noted that nickel chloride swells up in an ammonia soln. of **ammonium nitrate.** O. Lehmann reported the formation of solid soln. of nickel chloride with **ammonium chloride.** G. von Hüfner found that **nitric oxide** is absorbed by nickelous salts. J. J. Sudborough obtained no evidence of the formation of a complex salt with **nitrosyl chloride.** H. Rose observed that when nickel chloride is heated with **phosphorus,** nickel phosphide and phosphorus chloride are formed; and with **phosphine,** nickel phosphide and hydrogen chloride are produced. R. Scholder and H. L. Haken, and H. L. Haken also studied the action of phosphine on nickel salts. R. Schenck said that when a soln. of nickel chloride is poured into boiling potash lye, containing some phosphorus and tartaric acid, the phosphine which is developed furnishes nickel phosphide, Ni_4P_2, but if tartaric acid be absent, nickel oxyphosphide is formed. R. Scholder and co-workers, H. L. Haken, and C. Paal and L. Friederici found that an **alkali hypophosphite** precipitates nickel and nickel phosphide. E. Glatzel showed that **phosphorus pentasulphide** reacts in accord with the equation: $3NiCl_2 + 2P_2S_5 = Ni_3P_2S_8 + 2PSCl_3$.

J. H. Weibel studied the action of **carbon monoxide,** and L. Belladen and co-workers studied the equilibrium conditions in the reaction: $NiCl_2 + CO \rightleftharpoons Ni + COCl_2$, and, for $K = [CoCl_2]/[CO]$, they obtained approximately 0·0020 at 450°; 0·0070 at 500°; and 0·0086 at 550°. R. Tupputi noted that nickel chloride is soluble in **alcohol**; E. Bödtker added that 100 grms. of alcohol at room temp. dissolve 10·05 grms. of $NiCl_2$, and 53·71 grms. of $NiCl_2.6H_2O$; and C. A. L. de Bruyn, that 100 grms. of absolute alcohol dissolve 2·16 grms. of the hexahydrate at 17°, and 1·4 grms. at 3°. F. Mylius showed that when a gram of nickel chloride is dissolved in 100 c.c. of 10 per cent. hydrochloric acid, and shaken with 100 c.c. of **ether,** 0·01 per cent. of nickel enters into the ethereal layer. F. N. Speller studied the partition of the chloride between ether and dil. hydrochloric acid. K. P. MacElroy and W. H. Krug, and W. Eidmann observed that anhydrous nickel chloride is insoluble in **acetone.** O. Aschan noted that 100 grms. of 95 per cent. **formic acid** dissolve 5·9 grms. of $NiCl_2$ at 20·5°. S. Hakomori studied the action of **oxalic, citric, tartaric, malic, and succinic acids** on nickel salts. H. Frey observed that with **ethyl oxalate,** a trace of nickel carbonyl is formed; and S. Hakomori studied the formation of complex salts with tartaric acid. W. O. de Coninck found that 100 grms. of a sat. soln. in **glycol,** at room temp., contain 16·2 grms. of nickel chloride. G. Fuseya and K. Murata studied the action of **glycocoll.** J. V. Dubsky and A. Rabas did not obtain a compound with **glycine.** B. Köhnlein observed no marked reaction with **propyl iodide.** A. Naumann found that nickel chloride is sparingly soluble in **methyl acetate,** and insoluble in **ethyl acetate**; and H. Frey showed that when **ethyl oxalate** is added to finely-divided nickel chloride or bromide, and sodium, suspended in light petroleum, traces of nickel carbonyl appear in the gas which is evolved. P. Claesson found that an alcoholic soln. of nickel chloride forms nickel mercaptide, $Ni(SC_2H_5)_2$, when it is treated with mercaptan and ammonia. G. Walter, A. Werner and co-workers, and A. Rosenheim and V. J. Meyer found that yellowish-brown crystals of the complex salt $Ni_2(CH_4N_2S)_7Cl_2$, are formed with **thiourea.** W. Gluud and W. Riese studied the use of nickel salts in removing **hydrocyanic acid** from coke

and oven gas; and S. Papiermeister, the action of **mercuric cyanide** on nickel chloride. A. Naumann observed that nickel chloride is sparingly soluble in **benzonitrile**; and W. Eidmann, that it is insoluble in **methylal.** J. Ville and J. Moitessier studied the action of **phenylhydrazine.** P. Pfeiffer and co-workers prepared complex salts with naphthalene-1-sulphonic acid, naphthalene-2-sulphonic acid, benzene sulphonic acid, and *p*-toluene sulphonic acid, and complexes with tridipyridyl- and tri-phenanthrolin.

N. A. Kurnakoff, A. G. Berghman, F. Schürmann, J. Dalietos, W. R. Bucknall and W. Wardlaw, A. Werner and W. Spruck, and H. Grossmann and B. Schück studied the action of **ethylenediamine** on nickel chloride. They obtained **nickelous trisethylenediaminochloride,** $[Ni\ en_3]Cl_2.2H_2O$, by adding 3 mols. of ethylenediamine hydrate to a conc. soln. of a mol of nickelous chloride, evaporating the soln. for crystallization, and re-crystallizing the salt twice from its aq. soln. They did not succeed in preparing a chlorotartrate, but they prepared a tartrate, and a camphorsulphonate. They did not succeed in preparing an optically active form. J. Angerstein, and Y. Shibata investigated the absorption spectrum; O. Stelling, the X-ray spectrum; and E. Rosenbohm gave 12.87×10^{-6} mass unit for the magnetic susceptibility. W. R. Bucknall and W. Wardlaw attempted a resolution of the salt. T. Inoue studied the aquo-salts. Y. Shibata examined the absorption spectrum of **nickelous bisethylenediaminochloride,** $[Ni\ en_2]Cl_2.H_2O$; and G. and P. Spacu prepared **cadmium nickel trisethylenediaminochloride,** $[Ni\ en_3]CdCl_4$. F. G. Mann, M. Papafil, W. Hieber and co-workers, and A. Werner and J. Pastor studied the complex salts with **propylenediamine,** namely, **nickelous trispropylenediaminochloride,** $[Ni\ pn_3]Cl_2.2H_2O$, and E. Rosenbohm gave 11.46×10^{-6} mass unit for its magnetic susceptibility. J. Frejka and L. Zahlova prepared **nickelous trisbutylenediaminochloride,** $[Ni\ bn_3]Cl_2.H_2O$; and W. Hieber and K. Ries, **nickelous phenylenediaminochloride**; M. R. Menz, and J. C. Duff and E. J. Bills prepared complex-salts with **hexamethylenetetramine.** A hydroxychloride is also formed which reacts with the base to form $3Ni(OH)_2.N(CH_2.OH)_4$. O. Stelling studied the X-ray spectrum of **nickelous quater-o-phenylenediaminochloride,** $Ni(NH_2.C_6H_4.NH_2)_4Cl_2$. M. Poni, and R. Cernatescue and co-workers, studied compounds with the **cyclic amines**—$C_6H_3(CH_3)(NH_2)_2$, and $C_{10}H_6(NH_2)_2$. E. Beckmann said that nickel chloride is soluble in **quinoline,** and F. Reitzenstein, and U. Pomilio prepared a complex salt $Ni(C_9H_7N)_2.Cl_2$. G. Scagliarini and M. Ragno, and A. Werner studied the action of **piperidine** on nickel chloride; and E. Lippmann and G. Vortmann noted that complex salts are formed with **aniline,** and with **p-toluidine.** W. A. Redeker, and F. Reitzenstein studied the complex salts formed with **pyridine**; and O. Stelling, the X-ray spectrum of **nickelous quaterpyridinochloride,** $NiPy_4Cl_2$. G. T. Morgan and F. H. Burstall prepared **nickelous tris-αα′-dipyridylchloride,** $[Ni(C_{10}H_8N_2]Cl_2.6H_2O$. F. Paneth and E. Thilo, E. Thilo and H. Heilborn, K. Friedrich, and K. Kimura and H. Sueda prepared complexes with **diacetyldioxime,** and with **methyldiacetyldioxime**; G. Ponzio and I. de Paolini, a complex $[Ni(C_2H_2O_3N_2)_2]Cl_2$, with **hydroxyglyoxime**; W. Hieber and E. Levy, a complex with **monoethylolamine,** with **diethylolamine,** and with **triethylolamine**; K. A. Jensen and E. Rancke-Madsen, the complexes with **thiosemicarbazide;** O. S. Dumont and S. Pateras, with **indole,** $[Ni(C_8H_6)_4]Cl_2$; J. V. Dubsky and F. Brychta, a complex with **dimethylglyoxime**; W. Hieber and F. Leutert, complexes with **aldoximes,** and **ketoximes**; P. Pfeiffer and F. Tappermann, the **dipyridyl,** and **phenanthroline** addition products; F. Garelli and A. Tettamanzi, and A. Tettamanzi and B. Carli obtained **triethanolamine** addition product; H. Ruhlen and G. von Hühn, complexes with **ethyl sulphide**; G. Ponzi, a complex with **methylhydroxyglyoxime,** $[Ni(C_3H_6O_3N_2)_2]Cl_2$; and M. R. Menz, a complex with **camphidine**; but J. V. Dubsky and A. Rabas did not obtain a complex with **glycerine.** J. Roszkowsky noted that the presence of many organic substances hinders the precipitation of nickel hydroxide from soln. of nickel chloride.

W. Thomson and F. Lewis studied the action of **india rubber**; and H. Sobue and S. Manago, of **silk.** O. Hassel and H. Kringstad observed that the compound formed with **boron trifluoride,** namely, **nickel hexamminofluoborate,** $[Ni(NH_3)_6](BF_4)_2$, has a space-lattice with a=11·27 A.

D. Vitali observed that when **magnesium** acts on a soln. of a nickel salt, nickel hydroxide is formed, and that this is subsequently reduced by the hydrogen. E. S. Hedges and J. E. Myers, and G. Gire and A. M. de Narbonne studied the reaction. R. Müller and co-workers observed that **zinc,** and **cadmium** precipitate nickel from soln. of nickel chloride in absolute alcohol. C. Formenti and M. Levi studied the reducing action of **aluminium**; J. Cichocky, the diffusion of salt ions into aluminium. H. Moissan noted that a soln. of nickel chloride yields nickel amalgam (*q.v.*) when treated with **sodium amalgam.** T. Peczalsky observed that when nickel chloride is heated at 800° in an **iron** tube, a cementation product of iron and nickel appears in small crystals. O. L. Erdmann found that when sublimed nickel chloride is boiled for a long time with a soln. of **potassium hydroxide,** green nickel hydroxide is formed. J. A. Hedvall studied the action on alkaline earth-oxides; L. de Brouckère, the adsorption by **barium sulphate**; E. Montignie, the action of **mercuric oxide**; and H. O. Schulze, the action of nickel chloride on **tungstic acid.** N. N. Mittra and N. R. Dhar studied the influence of the salt on the oxidation reactions.

The double salts of nickel chloride.—R. Tupputi reported that hydrated **ammonium nickel trichloride,** $NH_4Cl.NiCl_2.6H_2O$, is formed from a mixed soln. of nickel and ammonium chlorides. O. Hautz obtained the salt by concentrating the mixed soln. by slow evaporation, and allowing it to stand in dry air for several days; and J. Adams and J. M. Merrick, by evaporating a mixed soln. of 2 mols. of nickel chloride and one mol. of ammonium chloride over sulphuric acid. B. Srebroff, A. Chassevant, H. Mitchell, and A. Johnsen employed a similar process. O. Hautz described the crystals as green, oblique prisms. A. Johnsen said that the monoclinic crystals have the axial ratios $a:b:c$=1·02293 : 1 : 0·70928, and B=89° 50′; and if rhombic, $a:b:c$=0·9786 : 1 : 0·68672. Twinning occurs about the (110)- and the (111)-faces; the optic axial angle $2H_a$ is 88° 35′ with Na-light. The double refraction is strong. The sp. gr. is 1·645. J. M. Merrick found that the electrolysis of the soln. furnishes nickel. O. Stelling and F. Olson studied the X-ray absorption spectrum. H. Moehle gave $2·001\times10^{-6}$ mass unit for the magnetic susceptibility. The crystals deliquesce in moist air, and they are freely soluble in water. They lose combined water at 135°. H. A. Frasch prepared **ammonium nickel hexamminochloride,** $(NH_4)_2Ni(NH_3)_6Cl_2$.

B. Srebroff, A. Neuhaus, A. C. D. Rivett and F. W. J. Clendinnen, O. Lehmann, S. M. Jörgensen, and J. W. Retgers observed that ammonium and nickel chlorides form solid soln. H. W. Foote inquired if a double salt is really formed at 25°, since, with soln. containing the following percentages of nickel and ammonium chlorides, the products were solid soln.—" n.d." means " not determined."

Solution	NH_4Cl	26·07	10·21	9·16	7·98	8·07	8·17	7·51	3·06
	$NiCl_2$	3·10	30·56	35·70	37·41	37·73	37·64	37·19	37·98
Solid	NH_4Cl	n.d.	75·79	55·59	43·62	34·67	16·03	tr.	tr.
	$NiCl_2$	0·32	17·37	32·06	39·40	44·03	48·93	54·64	54·04
	H_2O	n.d.	6·84	12·35	16·98	21·30	35·40	n.d.	n.d.
		Solid solution of $NH_4Cl+nNiCl_2.2H_2O$			Solid solution and $NiCl_2.2H_2O$			$NiCl_2.6H_2O$	

where the nickel salt is present as a dihydrate in the solid soln. The maximum amount of nickel chloride which can form a solid soln. with ammonium chloride is about 37 per cent. at 25°, but the limit probably varies with temp. The double salt can be obtained at temp. below 20° (approximately); above that temp., the double salt decomposes into a mixture of hexahydrated nickel chloride, and a solid soln. of the component salts. As in the case of cobalt chloride, there is

nothing to show whether or not some nickel chloride is united chemically with ammonium chloride so that the solid soln. consist of ammonium chloride associated with x of a double salt. F. W. J. Clendinnen's results for the ternary system: $NiCl_2$–NH_4Cl–H_2O at 70°, are summarized in Fig. 328. This temp. was chosen to avoid complications with the hydrates above $NiCl_2.2H_2O$. The following is a selection of the results—concentrations are expressed in percentages:

NH_4Cl	30·92	20·47	17·54	16·24	11·74	6·96	1·24
$NiCl_2$	8·59	26·28	30·69	32·30	36·99	42·05	45·60
NH_4Cl in solid .	98·3	84·6	62·5	48·0	34·8	25·9	0·1

There is no indication of the formation of a double salt at this temp. There are regions of metastability bounded by the dotted lines in the diagram. The compositions of the solid soln. are represented by points on the line *AD*, Fig. 328, which is continuous between ammonium chloride and dihydrated nickel chloride. The subject was studied by A. C. D. Rivett and F. W. J. Clendinnen. H. Franzen and H. L. Lucking obtained **hydrazine nickel tetrachloride,** $(N_2H_4.HCl)_2.NiCl_2.H_2O$, by mixing soln. of nickel chloride and hydrazine hydrochloride.

O. Stelling and F. Osson studied the X-ray spectrum of **potassium nickel trichloride,** $KNiCl_3.5H_2O$. R. Godeffroy prepared yellow **rubidium nickel tetra-**

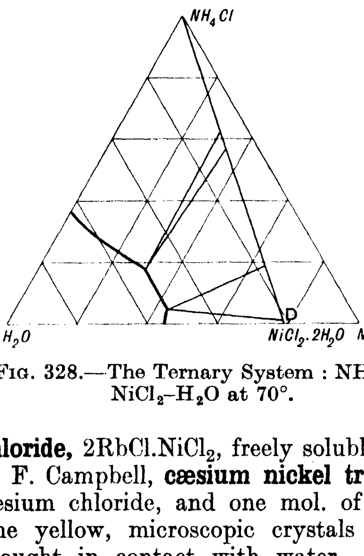

FIG. 328.—The Ternary System: NH_4Cl–$NiCl_2$–H_2O at 70°.

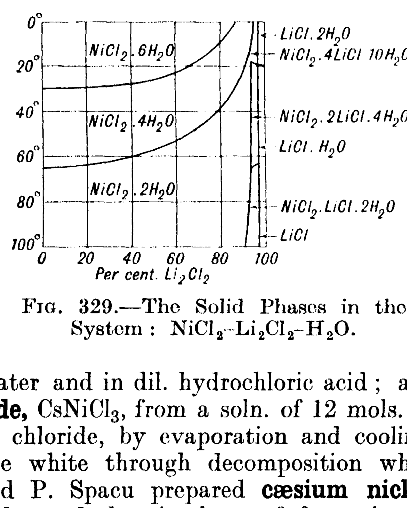

FIG. 329.—The Solid Phases in the System: $NiCl_2$–Li_2Cl_2–H_2O.

chloride, $2RbCl.NiCl_2$, freely soluble in water and in dil. hydrochloric acid; and G. F. Campbell, **cæsium nickel trichloride,** $CsNiCl_3$, from a soln. of 12 mols. of cæsium chloride, and one mol. of nickel chloride, by evaporation and cooling. The yellow, microscopic crystals become white through decomposition when brought in contact with water. G. and P. Spacu prepared **cæsium nickel amminotrichloride,** $Cs[NiCl_3].NH_3$, and observed that its heat of formation is 15·45 Cals., and it is stable at −78·5° for p=36 mm. At 0°, p=1·7 mm.; at 17·5°, p=3·6 mm.; and at 34·8°, p=12·0 mm. A. Chassevant also prepared hydrated **lithium nickel trichloride,** $LiNiCl_3.3H_2O$. H. Benraths's observations on the ternary system: $NiCl_2$–Li_2Cl_2–H_2O, are summarized in Figs. 329 and 330. There are three double salts, namely, lithium nickel hexachloride, $4LiCl.NiCl_2.10H_2O$, stable between 0° and about 23°; lithium nickel tetrachloride, $2LiCl.NiCl_2.4H_2O$, stable between 23° and 60°; and lithium nickel trichloride, $LiCl.NiCl_2.2H_2O$, stable above 60°.

A. Mailhe found that when a soln. of nickel chloride is treated with black cupric hydroxide, there is formed **copper nickel dioxychloride,** $2CuO.NiCl_2.6H_2O$, as a pale green, crystalline powder; but if blue cupric hydroxide is employed, hydrated **copper nickel trioxychloride,** $3CuO.NiCl_2.4H_2O$, or, according to A. Werner, $Cu_2(OH)_4Cu{=}(OH)_2{:}{:}{:}NiCl_2.H_2O$ is formed, and it is not decomposed by water. W. A. Endriss made observations on this subject.

C. von Hauer obtained dark green, deliquescent crystals of **cadmium dinickel hexachloride,** $CdCl_2.2NiCl_2.12H_2O$, by the spontaneous evaporation of a soln. containing 2 mols. of nickel chloride, and one mol. of cadmium chloride. The hexagonal crystals were found by J. Grailich to have the axial ratio $a : c=1 : 1·1750$. C. von Hauer also obtained **dicadmium nickel hexachloride,** $2CdCl_2.NiCl_2.12H_2O$, by treating a soln. of 3 mols. of nickel chloride and 2 mols. of cadmium chloride in a similar manner. An excess of nickel salt is necessary for the formation of this salt so that there is a difficulty in re-crystallizing the salt from water. The rhombic pyramids were found by J. Grailich to have the axial ratios $a:b:c=0·9126 : 1 : 0·3431$; the (100)-cleavage is incomplete; and the double refraction is positive. The pleochroic crystals have a and b pale green, and c, a deep sea-green. C. von Hauer found that the crystals effloresce over calcium chloride, and become white; they lose about 10 of the 12 mols. of water at 100°, and the last 2 mols. of water at 160° to 165°. When the salt is heated rapidly, it melts in its water of crystallization; and when more strongly heated, chlorine is given off. The salt is freely soluble in water. The system was studied by G. Spacu and E. Popper.

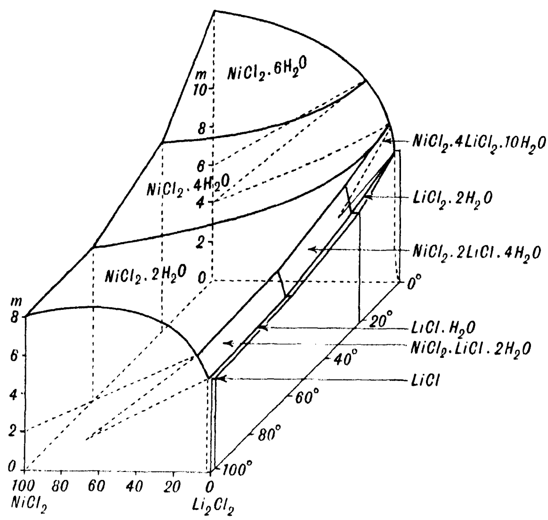

FIG. 330.—The Ternary System: $NiCl_2–Li_2Cl_2–H_2O$.

J. Gewecke prepared hydrated **thallic nickel octochloride,** $2TlCl_3.NiCl_2.8H_2O$, by allowing a soln. of the component salts, acidified with hydrochloric acid, to evaporate in vacuo over sulphuric acid. The bright green, deliquescent crystals can be re-crystallized from aq. soln. S. M. Jörgensen prepared hydrated **stannous nickel tetrachloride,** $SnCl_2.NiCl_2.6H_2O$, by concentrating a soln. of the component salts; and hydrated **stannic nickel hexachloride,** $SnCl_4.NiCl_2.6H_2O$, from soln. containing equimolar proportions of the compound salts. The green rhombohedra belong to the tetragonal system, and have the axial ratio $a:c=1:0·5048$, and $\alpha=112° 30'$. L. Pauling deduced from the X-radiograms that the space-lattice is a rhombohedron with $a=7·09$ A., and $\alpha=96° 45'$; and contains 1 mol. per unit cell. The structure, roughly, appears to be an arrangement of $[SnCl_6]$-complexes about a $[Ni(H_2O)_6]$-complex, as indicated in Fig. 331. The subject was discussed by O. Hassel. According to H. Töpsöe and C. Christiansen, the double refraction is weak; and the optical character, positive. S. M. Jörgensen gave 2·699 for the sp. gr.

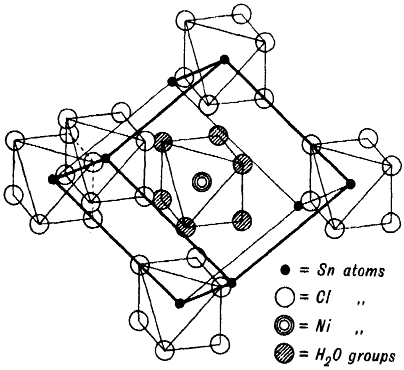

FIG. 331.—The Lattice Structure of Hexahydrated Nickelous Chlorostannate, $NiSnCl_6.6H_2O$.

Y. Osaka and T. Yaginuma studied the ternary system: $NiCl_2–FeCl_2–H_2O$ at

25°. They observed no evidence of the formation of a **ferrous nickel chloride.** Expressing the concentration of the sat. soln. in percentages, they found :

$FeCl_2$	0	9·26	16·25	21·56	21·65	29·82	35·26	39·61
$NiCl_2$	38·88	30·68	24·03	19·42	19·30	10·52	4·44	0
H_2O	61·12	60·06	59·72	50·02	59·05	59·66	60·30	60·39
		$(Fe,Ni)Cl_2.4H_2O$				$(Fe,Ni)Cl_2.6H_2O$		

The results are plotted in Fig. 332. There are two series of solid soln., respectively, $(Fe,Ni)Cl_2.4H_2O$, and $(Fe,Ni)Cl_2.6H_2O$.

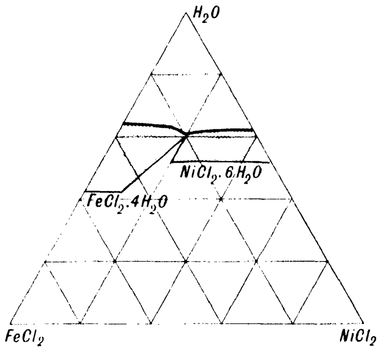

FIG. 332.—The Ternary System : $FeCl_2$–$NiCl_2$–H_2O at 25°.

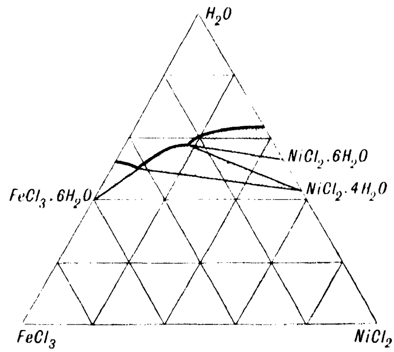

FIG. 333.—The Ternary System : $FeCl_3$–$NiCl_2$–H_2O at 25°.

Y. Osaka and T. Yaginuma studied the system : $FeCl_3$–$NiCl_2$–H_2O at 25°, and observed no sign of the formation of a **ferric nickel chloride.** Expressing the concentrations of sat. soln. in percentages, they found the results indicated in Fig. 333, and

$FeCl_3$	0	10·24	26·33	31·35	40·65	41·01	46·08	49·42
$NiCl_2$	38·88	30·89	19·86	16·43	10·73	10·01	4·37	0
Solid phases		$NiCl_2.6H_2O$		$NiCl_2.4H_2O$			$FeCl_3.6H_2O$	

Likewise for the system : $NiCl_2$–$CoCl_2$–H_2O, at 25°, Fig. 334. Y. Osaka and

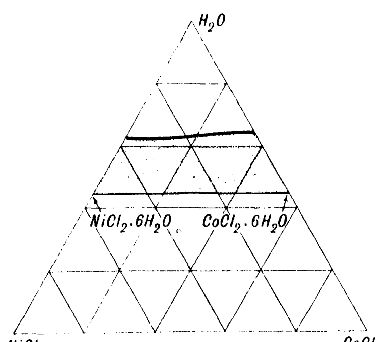

FIG. 334.—The Ternary System : $NiCl_3$–$CoCl_2$–H_2O at 25°.

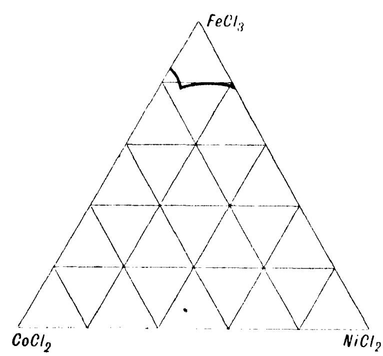

FIG. 335.—The Ternary System : $NiCl_2$–$CoCl_2$–$FeCl_3$ at 25°.

T. Yaginuma, and Y. Shibata and co-workers found for sat. soln. :

NiCl	38·88	34·36	30·63	22·51	10·45	4·31	0
$CoCl_2$	0	4·38	7·66	14·87	26·17	32·06	36·08
Solid phases	$NiCl_2.6H_2O$			Solid soln. $(Co,Ni)Cl_2.6H_2O$			$CoCl_2.6H_2O$

They also studied the quaternary system: $FeCl_3$–$CoCl_2$–$NiCl_2$–H_2O at 25°, and found for sat. soln.:

$FeCl_3$ . .	40·63	40·02	40·78	41·32	40·87	41·80	40·30
$NiCl_2$ . .	10·75	8·76	5·84	4·54	3·53	1·86	0
$CoCl_2$ . .	0	1·53	4·03	5·25	6·63	7·62	7·40
H_2O . .	48·62	49·69	49·35	48·98	48·97	48·73	52·30

The results for the three chlorides, calculated without water, are summarized in Fig. 335. S. Lussana and G. Bozzola studied the sp. gr. of mixed soln. of the two salts. A. G. Berghman studied **nickel cobaltic ethylenediaminochloride**, $\{[Co\ en_3]Cl_3\}_2NiCl_2$.

C. Schall and H. Markgraf [3] prepared **nickelic chloride** or **nickel trichloride**, $NiCl_3$, by dissolving nickel sesquioxide in conc. hydrochloric acid, or by the electrolysis of a soln. of nickelous chloride in hydrochloric acid.

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§ 15. Nickelous Bromide

J. B. Berthemot[1] found that nickel filings at a dull red-heat absorb bromine vapour and turn brown ; at a higher temp. the product, **nickel bromide,** $NiBr_2$, assumes the appearance of mosaic gold ; and at a bright red-heat, it partially

sublimes in yellow, micaceous scales. T. W. Richards and A. S. Cushman observed that some oxide is contaminated with the bromide when it is heated in hydrogen bromide; and F. Bourion found that if nickel oxide is heated in a current of hydrogen bromide containing a small proportion of sulphur monochloride nickel bromide is formed. The sulphur monochloride should be heated only to from 60° to 90° to supply the vapour required, and the hydrogen bromide should not be passed through the liquid. F. Ducelliez and A. Raynaud found that when dry bromine is added to finely-divided nickel, suspended in ether, and the resulting $NiBr_2.(C_2H_5)_2O$ is heated, anhydrous nickel bromide free from ether is obtained. T. W. Richards and A. S. Cushman obtained the salt of a high degree of purity by subliming it in a porcelain tube in a current of nitrogen mixed with hydrogen bromide. Since nickel bromide is decomposed by oxygen or water at a red-heat, a large excess of hydrogen bromide should be present. J. B. Berthemot prepared a soln. of nickel bromide by digesting nickel with bromine water; it can also be made by dissolving nickel hydroxide in hydrobromic acid. I. Bolschakoff found that the aq. soln. at temp. below −2·5° deposits the *enneahydrate*, $NiBr_2.9H_2O$; and at 20° or below 28·5°, the *hexahydrate*, $NiBr_2.6H_2O$; and above that temp., say at 58°, the *trihydrate*, $NiBr_2.3H_2O$. When the green aq. soln. is concentrated, and allowed to crystallize at ordinary temp., the trihydrate appears in deliquescent needles. P. Kusnetzoff prepared a *dihydrate*.

J. A. A. Ketelaar found that the hexagonal lattice has a=3·71 A., and c=18·30 A., or if rhombohedral, a=6·46, and c=16° 40′; and there is another structure with a=2·11 A., c=6·08 A., and sp. gr. 5·45. V. M. Goldschmidt and co-workers discussed the lattice structure. T. W. Richards and A. S. Cushman observed that the colour of the sublimed bromide varies from a pale straw-yellow to a dark bronze-brown, according to the state of aggregation. They found the sp. gr. to be 4·64 at 28°/4°; W. Biltz and E. Birk gave 5·042 at 25°/4°, and for the mol. vol., 43·34—measured with toluene. F. Ephraim and O. Schütz discussed the mol. vol., and the contraction which attends the formation of the compound from its elements. A. Heydweiller gave for the sp. gr. of aq. soln. at 18°:

$NiBr_2$.	4*N*-	3*N*-	2*N*-	*N*-	0·5*N*-	0·2*N*-	0·1*N*-
Sp. gr. .	1·3840	1·2897	1·1945	1·0981	1·0492	1·0198	1·0099

E. Beckmann found that the mol. wt., calculated from raising of the b.p. of quinoline soln., is normal. K. Jellinek and R. Uloth studied the dissociation press. According to I. Bolschakoff, the enneahydrate melts undecomposed at −2·5°; and the hexahydrate at 28·5° at which temp. it passes into the trihydrate. The green crystals of the trihydrate were found by C. F. Rammelsberg to lose water and become yellow when confined over sulphuric acid; at 200°, practically all the water of hydration is expelled. According to W. Fischer and R. Gewehr, the m.p. is 963; J. Thomsen gave for the heat of formation from liquid bromine in aq. soln., $(Ni,Br_2,Aq.)$=71·82 Cals. G. Denigès, H. Fesenfeldt, J. Gielessen, and W. N. Hartley studied the absorption spectrum; P. Job, the colour; and R. W. Roberts, the magnetic rotatory power. G. Crut gave 36·9 Cals. for the heat of the reaction: $NiBr_2+H_2 \rightleftharpoons Ni+2HBr$. The heat of formation of the anhydrous bromide from bromine gas is 61·5 Cals.; and the heat of soln. of the anhydrous salt is 18·9 Cals. The subject was discussed by F. Ephraim; and the energy of the molecule, by G. Beck. A. Heydweiller found the eq. electrical conductivity, λ, of aq. soln. at 18° to be

$NiBr_2$ . . .	4*N*-	3*N*-	2*N*-	*N*-	0·5*N*-
λ	37·5	45·1	54·5	65·8	73·4

For soln. of a mol. of the salt in v litres, at 25°, W. Althammer gave:

v	20	80	320	1280	5120
λ	99·8	110·3	118·8	124·3	127·6

and for $0{\cdot}05M$- and $0{\cdot}01M$-soln., he reported, respectively, the percentage hydrolysis 0·22 and 0·82. W. Isbekoff studied the decomposition potential of soln. of nickel bromide in fused zinc or aluminium bromide. O. Liebknecht and A. P. Wills gave 20×10^{-6} mass unit for the magnetic susceptibility of an aq. soln. at 18° ; A. Serres studied the subject.

G. Crut found that the reduction of nickel bromide by hydrogen is a reversible reaction, and the value of the equilibrium constant over the range 445° to 575° is 12·5. According to J. B. Berthemot, the trihydrate readily deliquesces when exposed to air to form an aq. soln. ; the sublimed bromide deliquesces much more slowly. T. W. Richards and A. S. Cushman found that freshly-sublimed nickel bromide, exposed to the air of a room, absorbed about 0·1 mgrm. per gram in 10 mins. J. B. Berthemot observed that nickel bromide, at a bright red-heat, forms nickel oxide and bromine ; and H. O. Schulze added that when heated in oxygen, nickel bromide is more or less completely transformed into the oxide. T. W. Richards and A. S. Cushman found that, in subliming the salt in a current of hydrogen bromide and nitrogen, at a red-heat, if traces of air or moisture be present, more or less green nickelous oxide will be formed unless an excess of hydrogen bromide be present. W. N. Hartley studied the deliquescence of the salt. T. W. Richards and A. S. Cushman found that sublimed nickel bromide dissolves so very slowly in water at ordinary temp. that it is said to be " insoluble " ; but in water at 50°, the salt dissolves more quickly ; and at 90°, a gram requires an hour or two for complete dissolution. The presence of nitric acid does not appreciably hasten the dissolution. The hydrates dissolve rapidly in water. If the sublimed oxide is free from oxide, the soln. is clear even at its b.p. A. Étard gave for the percentage solubility, S, of nickel bromide :

	−21°	−6°	19°	38°	58°	77°	98°	100°	140°
S . .	47·1	51·7	56·6	58·9	60·5	60·3	61·0	61·0	60·7 per cent.

The equilibrium conditions of the different hydrates—*vide supra*—have not been worked out. F. Förster and K. Georgi studied the deposition potential of nickel from soln. of the bromide—*vide supra*. W. Isbekoff studied the decomposition potential of the bromide in fused zinc bromide ; W. Klemm and W. Schüth, and S. S. Shaffer and N. W. Taylor studied the magnetic properties ; W. Klemm and W. Schüth found the magnetic susceptibility to be $\chi\times10^6=118$ at 90° K. ; 42·5 at 195° K. ; 26·0 at 293° K. ; and 10·1 at 643° K. ; and B. Cabrera and A. Duperier studied the action of temp. on the magnetic susceptibility.

According to J. B. Berthemot, an aq. soln. of nickel bromide left in contact with air deposits flakes of an oxide. T. W. Richards and A. S. Cushman observed no evidence of this, and attributed the results to the presence of a slight admixture of oxide with the bromide. J. B. Berthemot found that the salt is soluble in hydrochloric acid, and that it is decomposed by nitric acid.

C. F. Rammelsberg found that powdered nickel bromide vigorously absorbs dry ammonia to form a pale violet powder of **nickelous hexamminobromide,** $NiBr_2.6NH_3$, and when a conc. aq. soln. of nickelous bromide is warmed with an excess of aq. ammonia, the soln. deposits a blue crystalline powder on cooling. T. W. Richards and A. S. Cushman added that a similar compound is not formed by cobalt or by many other metals, under similar circumstances, and since it is soluble in hot, conc. aq. ammonia, but almost insoluble in cold aq. ammonia, it affords " a convenient and effectual means of purifying nickel preparations." P. Groth said that the octahedral crystals are singly-refracting. R. W. G. Wyckoff added that crystals are isomorphous with those of ammonium chloroplatinate, which have a face-centred, cubic space-lattice of the calcium fluoride type with 4 mols. per unit cell, and $a=10{\cdot}48$ A.—*vide supra*, nickelous hexamminochloride. G. B. Naess and O. Hassel studied the lattice structure and found $a=10{\cdot}34$ A., and gave for the distance between the Ni and Br atoms, 4·48 A. ; they also studied the sphere of action of the anion. Likewise with A. Ferrari and F. Giorgi.

W. Biltz and E. Birk gave a=10·39 A., and found 1·889 for the sp. gr. at 25°/4°, and 169·8 for the mol. vol. S. G. Mokruschin and E. I. Kriloff studied the surface energy. W. Biltz, and W. Biltz and B. Fetkenheuer observed the following values for the dissociation press., p mm., and the heat of dissociation, Q Cals., at different temp.:

	84·5°	117°	158·5°	174°	198°	206°	213°
p . . .	4	9	73	161·5	487	708	828
Q . . .	16·4	17·4	17·6	17·6	17·6	18·0	17·7

The subject was discussed by E. Kocsis, G. Beck, G. L. Clark, W. Hieber and E. Levy, F. Ephraim, and F. Ephraim and O. Schütz. R. Samuel and co-workers studied the absorption spectrum. R. Robl observed no luminescence with the hexammine in ultra-violet light. F. Ephraim and P. Mosimann, and P. Mosimann found the solubility in water to be 7·38 grms. or 0·023 mol per litre. The dissociation of the hexammine: $NiBr_2.6NH_3 \rightleftharpoons NiBr_2.2NH_3 + 4NH_3$, furnishes **nickelous diamminobromide,** $NiBr_2.2NH_3$, whose dissociation press., p mm., and heats of dissociation, Q Cals., are:

	195°	236°	278°	295°	309°	325°	356°
p . . .	2	14	81	142·5	191	321·5	709
Q . . .	22·5	22·7	22·8	23·0	23·2	23·3	23·7

The results are plotted in Figs. 336—*vide supra*, Figs. 326 and 327. At 760 mm. press., and 352°, the diammine dissociates: $NiBr_2.2NH_3 \rightleftharpoons NiBr_2.NH_3 + NH_3$; and the resulting **nickelous amminobromide,** $NiBr_2.NH_3$, has a very narrow range of stability, Fig. 336. The dissociation press. given by W. Biltz are 59·7 mm. at 276°; 121 mm. at 299°; and 381 mm. at 336°. W. Biltz and G. F. Hüttig gave 15·35 Cals. per NH_3-mol. for the heat of formation of the hexammine; 20·40 Cals. for the diammine; and 20·78 Cals. for the monammine. E. Rosenbohm found the magnetic susceptibility of the hexammine to be $13·89 \times 10^{-6}$ mass unit. W. Klemm and W. Schüth, and S. S. Shaffer and N. W. Taylor studied the subject. C. F. Rammelsberg observed that the hexammine furnishes nickel bromide when it is heated; and that it forms a blue soln. with a small proportion of water, and with an excess of water, nickelous hydroxide is precipitated, but the soln. remains pale blue.

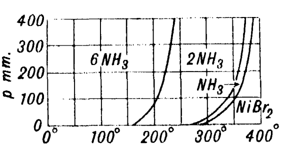

FIG. 336.—The Dissociation Pressures of the Nickelous Amminobromides.

H. Franzen and O. von Mayer found that when a hot aq. soln. of nickel bromide is mixed with a hot, 50 per cent. soln. of hydrazine hydrate, a bluish-white precipitate is formed, which when washed with water, and fused, in vacuo, furnishes **nickelous dihydrazino bromide,** $NiBr_2.2N_2H_4$. The bluish-white powder is freely soluble in aq. ammonia and dil. acids. If 20 grms. of nickel hexamminobromide are warmed on a water-bath with 40 c.c. of 50 per cent. hydrazine hydrate, ammonia is given off, and a reddish-violet crystalline precipitate is deposited which when washed successively with water, alcohol, and ether, and dried in vacuo, furnishes **nickelous trihydrazinobromide,** $NiBr_2.3N_2H_4$. The salt forms a green soln. with dil. acids. The air-dried salt shows signs of decomposition in a couple of days; and when heated it gives off hydrazine, and leaves behind anhydrous nickel bromide. H. Franzen and H. L. Lucking obtained **hydrazine nickelous tetrabromide,** $NiBr_2(N_2H_4.HBr)_2.4H_2O$, by mixing soln. of nickel bromide and hydrazine hydrobromide.

According to H. Frey, when ethyl oxalate is added to freely-divided nickel bromide and sodium, suspended in ligroin, traces of nickel tetracarbonyl are formed. J. B. Berthemot observed that nickel bromide is insoluble in alcohol, and ether; T. W. Richards and A. S. Cushman, that it is insoluble in toluene; E. Beckmann, that it is soluble in quinoline; and A. Naumann, that it is slightly soluble in

benzonitrile. E. Schürmann, J. Dalietos, and A. Werner and W. Megerle obtained complexes with nickel bromide and ethylenediamine analogous to those obtained with the chloride, namely, **nickel trisethylenediaminobromide,** $[Ni\,en_3]Br_2$; and G. and P. Spacu prepared **cadmium nickel trisethylenediaminobromide,** $[Ni\,en_3]CdBr_4$. A. Werner and J. Pastor obtained a complex with propylenediamine, namely, **nickel trispropylenediaminobromide,** $[Ni\,pn_3]Br_2$; J. Frejka and L. Zahlova, a complex with butylenediamine, namely, **nickel trisbutylenediaminobromide,** $[Ni\,bn_3]Br_2.H_2O$; W. Hieber and K. Ries, a complex with **o-phenylenediamine**; W. Hieber and E. Levy, complexes with **monoethylolamine,** with **diethylolamine,** and with **triethylolamine**; A. Tettamanzi and B. Carli, a complex with **triethenolamine**; J. V. Dubsky and F. Brychta, a complex with **dimethylglyoxime**; M. Poni, compounds with **cyclic amines**—$C_6H_3(CH_3)(NH_2)_2$, and $C_{10}H_6(NH_2)_2$; G. Scagliarini and M. Ragno, compounds with **pyridine**; R. Varet, with pyridine; M. R. Menz, with **camphidine**; and H. Grossmann and F. Hünseler, with **phenylhydrazine.** G. T. Morgan and F. H. Burstall prepared **nickel tris-αα′-dipyridylbromide,** $[Ni(C_{10}H_8N_2)_3]Br_2.6H_2O$; and F. G. Mann and W. J. Pope, **nickel bistriaminotriethylenebromide,** $[Ni\{N(C_2H_4.NH_2)_3\}_2]Br_4$. W. Hieber and F. Leutert obtained complexes with **aldoximes** and **ketoximes**; P. Pfeiffer and F. Tappermann, with **phenanthroline.** Nickel bromide is insoluble in **ether,** and K. Schwenzer found that no reduction occurs with **magnesium,** in contact with the bromide in ether. J. A. Hedvall studied the action on the **alkaline earth oxides.**

G. F. Campbell prepared **cæsium nickel tribromide,** $CsNiBr_3$, from a soln. of 12 mols. of cæsium bromide and a mol. of nickel bromide. It has properties similar to those of the corresponding chloride (*q.v.*). A. Mailhe obtained green, hexagonal plates of **copper nickel trioxybromide,** $3CuO.NiBr_2.4H_2O$, or, according to A. Werner, $Cu_2(OH)_4Cu{=}(OH)_2{::::}NiBr_2.H_2O$, by the action of a cold soln. of nickel bromide on cupric oxide. R. Varet found that the heat of formation of **mercuric nickel bromide,** $2HgBr_2.NiBr_2$, is 3·10 Cals. at 18°, and of $NiBr_2.HgBr_2$, 2·81 Cals. A. Mailhe observed that mercuric nickel oxybromide, $6NiO.NiBr_2.HgBr_2.20H_2O$, is formed as a green powder when a soln. of nickel bromide acts on mercuric oxide. B. A. Isbekoff and W. A. Plotnikoff said that nickelous bromide is insoluble in aluminium bromide, and J. Kendall and co-workers observed a slight solubility, but no **aluminium nickel bromide** is formed. F. T. Frerichs and E. F. Smith prepared **didymium nickel bromide,** $2DiBr_3.3NiBr_2.18H_2O$, in reddish-brown, hygroscopic needles from a soln. of the component salts; and also **lanthanum nickel bromide,** $2LaBr_3.3NiBr_2.18H_2O$, in a similar manner. B. Rayman and K. Preis cooled a mixed soln. of stannic and nickel bromides, and obtained apple-green, deliquescent crystals of **stannic nickel bromide,** $NiSnBr_6.8H_2O$. G. Spacu and J. Dick prepared complex salts with hexamethylenetetramine, $Ni\,hm_6[SnBr_6]$; with pyridine, $Ni\,py_6[SnBr_5OH]$, and $Ni\,py_6[SnBr_6]$; and piperazine, $Ni\,pi_3[SnBr_6].8H_2O$; $Ni\,pi_4[SnBr_6].8H_2O$; and $Ni\,pi_6[SnBr_6].8H_2O$.

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§ 16. Nickelous Iodide

O. L. Erdmann [1] observed that if nickel powder, reduced by hydrogen, is heated with iodine in a glass tube, or if the vapour of iodine is passed over the heated metal, a mixture of nickel and nickel iodide is produced—if traces of air be present, some nickel oxide is formed as well. If this mixture is strongly heated out of contact with air, a black sublimate of **nickelous iodide**, NiI_2, is formed. Compact nickel is scarcely attacked when heated with iodine. M. Guichard obtained nickel iodide by arranging nickel wire and iodine in a glass tube so that they are separated by an asbestos plug, and then evacuating and sealing the tube. If the tube is heated so that the iodine is kept at about 180°, and the nickel at 500°, nickel iodide is formed as a sublimate of dark grey laminæ. According to C. F. Rammelsberg, and O. L. Erdmann, when a soln. of nickel hydroxide in hydriodic acid is evaporated, it furnishes crystals of the hexahydrate, $NiI_2.6H_2O$; and if the aq. soln. be evaporated to dryness, the black residue when heated out of contact with air, sublimes without fusion or decomposition. J. L. Lassaigne

heated a mixture of iodine and nickel, and observed that the brown product dissolves in water, forming a green soln. of nickel iodide.

Sublimed nickel iodide, said O. L. Erdmann, presents "the appearance of strongly lustrous, iron-black laminæ, resembling mica, and unctuous to the touch." J. A. A. Ketelaar found that the hexagonal crystals have a=3·89 A., and c=19·63 A., and if rhombohedral, a=6·92 A., and α=16° 20′. W. Biltz and E. Birk gave 5·834 for the sp. gr. at 25°/4°, and 53·57 for the mol. vol. K. Jellinek and R. Uloth studied the dissociation press. W. Fischer and R. Gewehr gave 797° for the m.p.; and J. Thomsen, $(Ni,I_2,Aq.)$=41·4 Cals. for the heat of formation. The subject was discussed by E. Rabinowitsch and E. Thilo, and F. Ephraim and O. Schütz. G. Denigès, H. Fesenfeldt, and W. N. Hartley studied the absorption spectrum. W. Riedel gave for the electrical conductivity of a soln. of a mol. of the salt, μ, in v litres at 25°, and for the degree of ionization, α,

v . . .	20	80	320	1280	5120	∞
μ . . .	100·29	109·51	117·22	122·72	130·20	128·99
α . . .	0·777	0·852	0·909	0·951	1·00	1·00

W. Althammer calculated for 0·05M- and 0·01M-soln. the respective percentage hydrolyses 0·04 and 0·15. According to W. Riedel, the transport numbers of the anions for soln. with v=21·5 and 300 are, respectively, 0·6384 and 0·6040; and for the cations, 0·3616 and 0·3960. For 0·05M- and 0·01M-soln., the H˙-ion concentrations are, respectively, $10^{-5.72}$ and $10^{-5.81}$; and the e.m.f. of the cell $(Pt)H_2 \mid NiI_2 \mid KCl_{sat.\ soln.} \mid 0{\cdot}1N\text{-}KCl.Hg_2Cl_2 \mid Hg$, with 0·05$M$- and 0·01$M$-$NiI_2$, are, respectively, 0·675 and 0·684 volt. W. Klemm and W. Schüth found the magnetic susceptibility $\chi \times 10^6$=26 at −183°; 17·3 at −78°; 125 at 20°; 7·50 at 220°; and 6·73 at 295°. B. Cabrera and A. Duperier studied the effect of temp.

According to O. L. Erdmann, if air has access to the salt during sublimation, or if the salt be heated in air, it forms greyish-green nickel oxide free from iodine. H. O. Schulze also noted that the iodide is converted into oxide when it is heated in air. When nickel iodide is exposed to air it deliquesces forming a reddish-brown liquid, which, on dilution, becomes green. The hydrated iodide is also deliquescent. W. N. Hartley studied the deliquescence of the salt. A. Étard found that sat. aq. soln. of nickel iodide contain:

	−23°	−6°	11°	16°	43°	80°	85°	90°
NiI_2 .	51·8	54·3	57·8	59·0	64·1	65·0	65·2	65·7 per cent.

O. L. Erdmann observed that when the aq. soln. is evaporated to dryness, and the residue extracted with water, there remains a reddish-brown powder; some of the residue may dissolve along with nickel iodide to form a brownish-green instead of a green soln. The soln. then smells of iodine, imparts a blue colour to starch, and gives off iodine when evaporated. A brownish-red liquid is obtained by digesting an aq. soln. of nickel iodide with nickel hydroxide, or nickel carbonate —in the latter case, carbon dioxide is given off. The reddish-brown liquor is also formed when nickel hydroxide is triturated with an alcoholic soln. of iodine. The reddish-brown powder is considered to be a basic salt, **nickelous enneaoxydiiodide,** $9NiO.NiI_2.15H_2O$. It decomposes at a red-heat giving off iodine and water vapour, and leaving a residue of nickel oxide; it dissolves in nitric acid with the evolution of iodine; alkali lye extracts the whole of the iodine; aq. ammonia changes the colour of the powder a dingy green, and the liquid becomes blue; boiling alcohol converts it into the green hydrated oxide, it forms a yellowish-green soln. with acetic acid; and oxalic acid transforms it into nickel oxalate. There is nothing here to establish the chemical individuality of the oxyiodide; the reddish-brown liquor is presumably hydrated nickel oxide peptized by the soln. of nickel iodide.

O. L. Erdmann, and R. G. van Name and W. G. Brown said that the aq. soln. of nickel iodide can dissolve a large proportion of iodine, forming a brown liquor containing presumably **nickel polyiodide,** and giving off the excess of iodine when

boiled. W. Riedel found that iodine reacts with the iodide, forming nickelous polyiodide, probably NiI_4, in aq. soln., and the conductivity corresponding with a soln. containing a mol of NiI_4 in v litres, at 25°, and the degrees of ionization, a, are:

v	20	80	320	1280	5120	∞
μ	88·85	98·50	106·55	114·04	115·0	119·03
α	0·747	0·828	0·895	0·958	0·966	—

R. F. Weinland and F. Schlegelmilch obtained siskin-green needles of **nickel octochloroiodide,** $NiCl_2.2ICl_3$, by the action of iodine on a soln. of nickel chloride. Iodine trichloride is removed by digesting the salt with carbon tetrachloride. L. Tschugaeff studied complex salts of bivalent metals and organic disulphides. According to O. L. Erdmann, A. Agrestini, and C. F. Rammelsberg, when a sat. aq. soln. of nickel iodide is treated with conc. ammonia, white flakes are formed which dissolve slowly when the liquid is warmed to form a reddish liquid which afterwards becomes light blue. When the blue soln. is cooled, or mixed with alcohol, it is decolorized and deposits a pale blue, crystalline powder of **nickelous hexamminoiodide,** $NiI_2.6NH_3$, consisting of octahedra belonging to the cubic system. P. Groth also said that the crystals are probably cubic. R. W. G. Wyckoff observed that the X-radiograms correspond with a face-centred lattice of the calcium fluoride type, isomorphous with the lattice of ammonium chloroplatinate. The length of unit cell is a=11·01 A., and there are 4 mols. per unit cell. G. B. Naess and O. Hassel studied the lattice structure, and gave a=10·875 A., and found the distance between the nickel and iodine atoms to be 4·71 A.; they also studied the sphere of action of the anion. W. Biltz and E. Birk gave a=10·90 A., and found the sp. gr. to be 2·113 at 25°/4°, and the mol. vol. 196·3. The mol. vol. was also studied by W. Biltz, and F. Ephraim. The surface energy was discussed by S. G. Mokruschin and E. I. Kriloff. F. Ephraim gave for the dissociation press., p mm., of the hexammine:

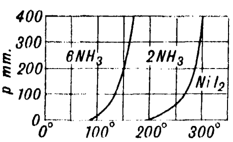

FIG. 337.—The Dissociation Pressure of Nickelous Amminoiodides.

	170°	182°	195°	205°	220°	225·5°	234°
p	84	125	195	275	470	565	720

The results are summarized in Fig. 337—*vide supra*, Fig. 327. The subject was discussed by G. L. Clark. For p=760 mm., W. Biltz and B. Fetkenheuer gave the dissociation temp. 235·5°. F. Ephraim and P. Mosimann found the solubility in water to be 1·91 grms. or 0·0046 mol. per litre. The product of the dissociation of the hexammine is **nickelous diamminoiodide,** $NiI_2.2NH_3$, which, according to W. Biltz and B. Fetkenheuer, has a dissociation press., p mm.,

	179°	206°	242°	253°	276·5°	302°	322·5°
p	3·6	9·5	43·5	66	127	326·5	575·5

and for p=760°, the dissociation temp. is 333°. The dissociation of the diammine furnishes nickel iodide, and there is no evidence of the formation of a monammine. According to W. Biltz and B. Fetkenheuer, the heat of formation of the hexammine is 18·5 Cals. per NH_3-mol., and for the diammine, 22·0 Cals. per NH_3-molecule. W. Biltz and G. F. Hüttig gave 15·94 Cals. per NH_3-mol., and 19·68 Cals. for the diammine. The subject was discussed by F. Ephraim, F. Ephraim and O. Shütz, E. Kocsis, and W. Hieber and E. Levy. The colour of the hexammine is bluish-violet, that of the diammine is brown, and that of the anhydrous iodide is black. W. Klemm and W. Schüth studied the magnetic properties of the ammines. J. A. Hedvall investigated the action of heat on mixtures with the **alkaline earth oxides.**

H. Franzen and H. L. Lucking prepared yellow **nickel dihydrazinoiodide,** $NiI_2.2N_2H_4$, by the action of hydrazine iodide or hydrate on nickel iodide.

J. Moitessier obtained a complex with phenylhydrazine. B. Köhnlein observed no marked reaction with **propyl chloride.** A. Werner, A. Werner and W. Megerle, and E. Schürmann studied the complexes formed with ethylenediamine, namely, **nickel trisethylenediaminoiodide,** $[Ni\ en_3]I_2$, analogous with those obtained with the chloride (*q.v.*), and G. and P. Spacu obtained **cadmium nickel trisethylenediaminoiodide,** $[Ni\ en_3]CdI_3$, and **lead nickel trisethylenediaminoiodide,** $[Ni\ en_3](PbI)_2$. A. Werner and J. Pastor prepared **nickel trispropylenediaminoiodide,** $[Ni\ pn_3]I_2$; J. Frejka and L. Zahlova, **nickel trisbutylenediaminoiodide,** $[Ni\ bn_3]I_2.4H_2O$; G. T. Morgan and F. H. Burstall, **nickel tris-αα′-dipyridyliodide,** $[Ni(C_{10}H_8N_2)_3]I_2.6H_2O$; and F. G. Mann and W. J. Pope, **nickel bistriaminopropanoiodide,** $[Ni(NH_2.CH_2.CH.NH_2.CH_2.NH_2]I_2$; **nickel bistriaminotripropylaminoiodide,** $[Ni\{N(C_3H_6.NH_2)_3\}_2]I_2.1\frac{1}{2}H_2O$; **nickel bistriaminotripropylaminohydroxyiodide,** $[Ni\{N(C_3H_6.NH_2)_3\}_2]I(OH).2H_2O$, and a complex salt with potassium iodide ; W. Hieber and co-workers, a complex with **o-phenylenediamine,** and **nickel bistriaminotriethylenoiodide,** $[Ni\{N(C_2H_4.NH_2)_3\}_2]I_4.3\frac{1}{2}H_2O$. M. R. Menz studied the complex formed with camphidine ; W. Hieber and K. Ries, a complex with **o-phenylenediamine ;** J. V. Dubsky and F. Brychta, a complex with **dimethylglyoxime ;** W. Hieber and F. Leutert, complexes with **aldoximes** and **ketoximes ;** W. Hieber and E. Levy, complexes with **monoethylolamine,** with **diethylolamine,** and with **triethylolamine ;** F. Garelli and A. Tettamanzi, complexes with triethanolamine; and C. Moureau and C. Dufraisse, the catalytic effect of nickel iodide on the oxidation of acrolein.

G. F. Campbell did not succeed in making **cæsium nickel iodide** by the process he employed for the corresponding chloride and bromide. G. Spacu prepared **nickel cadmium trisethylenediaminoiodide,** $[Ni\ en_3]CdI_4$. D. Dobroserdoff obtained **mercuric nickel hexaiodide,** $2HgI_2.NiI_2.6H_2O$, by evaporating, in vacuo, a soln. of the component salts. The dirty green, hygroscopic prisms readily lose water of hydration ; the salt is decomposed by water ; it is soluble in acetone, and alcohol ; and with ether, it forms two layers. If the mother-liquor obtained in the preparation of this salt be evaporated, it furnishes greyish-green crystals of **mercuric nickel tetraiodide,** $HgI_2.NiI_2.6H_2O$, which are not decomposed by water ; and they are soluble in alcohol, and ether. F. Ephraim and P. Mosimann reported **mercuric nickel amminoiodides:** $[Ni(NH_3)_4]I_2.HgI_2.4H_2O$; $[Ni(NH_3)]_6I_2.HgI_2.8H_2O$; $[Ni(NH_3)_4]I_2.HgI_2.2H_2O$; and $[Ni(NH_3)_6]I_2.HgI_2.8H_2O$. A. Mosnier prepared **lead nickel hexaiodide,** $PbI_2.2NiI_2.3H_2O$, by saturating with lead iodide a boiling, conc. soln. of nickel iodide, and evaporating in vacuo. The greenish needles are decomposed by water. The thermal value of the reaction $(PbI_2,2NiI_2)=40{\cdot}2$ Cals. ; $(PbNi_2I_4,2H_2O)=51{\cdot}3$ Cals. with liquid water ; and the heat of soln. of one part of $PbI_2.2NiI_2.3H_2O$ in 40 parts of water is $-11{\cdot}1$ Cals.

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§ 17. Nickel Sulphides

M. von Orlowsky,[1] O. Schurmann, E. F. Anthon, W. Guertler, E. V. Britzke and A. F. Kapustinsky, and E. Schürmann discussed the relative affinity of sulphur for the metals of the iron group. J. L. Proust, and H. Rose observed that sulphur and nickel combine with incandescence when they are heated together; and G. C. Winkelblech added that combination begins at a temp. below 115°. He also showed that nickel dust takes fire when projected into sulphur vapour; and a mixture of nickel dust and flowers of sulphur, in equivalent proportions, takes fire when touched at one end with a glowing coal.

According to J. A. Arfvedson, if hydrogen be passed over red-hot nickel sulphate, **nickel hemisulphide,** Ni_2S, is formed; sulphur dioxide and water are at first evolved, and later on, hydrogen sulphide. H. Rose obtained the hemisulphide by heating a mixture of hydrated nickel sulphide or dry nickel sulphate and sulphur in a current of hydrogen. A. Mourlot obtained it by reducing nickel sulphate mixed with carbon in an electric arc furnace; P. Berthier, by heating nickel sulphate in a carbon crucible at a white-heat; A. Gautier and L. Hallopeau, by heating nickel at a white-heat in a current of carbon disulphide; and R. Schneider, by melting a mixture of nickel sulphate with six times its weight of potassium carbonate and sulphur. J. P. Podolsky and N. M. Zarubin said that it is formed when sulphur acts on nickel below 600°. R. Scheuer regarded the hemisulphide as a solid soln. of nickel in the monosulphide. According to H. Rose, the pale yellow, or brass-yellow mass is not magnetic; L. Playfair and J. P. Joule gave 6·05 for the sp. gr., and A. Mourlot, 5·52. According to A. Gautier and L. Hallopeau, its sp. gr. is 5·66 at 0°; it is not decomposed by hot or cold water; it is attacked with difficulty by hydrochloric acid when it gives off hydrogen sulphide and hydrogen. The prolonged action of heated carbon disulphide converts the hemisulphide into monosulphide. J. A. Arfvedson added that it dissolves in nitric acid with the separation of sulphur. There is nothing in all this to disprove the contra-suggestion that the alleged nickel hemisulphide is the product of arrested reactions. H. le Chatelier and A. Ziegler consider that the product of the action of the metal on the sulphide is a simple mixture. K. Bornemann added that whilst nickel hemisulphide does not appear to be capable of separate existence, it can form a stable compound with ferrous sulphide—*vide infra*.

G. Masing and L. Koch observed a eutectic with nickel and nickel sulphide, Ni–Ni_3S_2, at 625°. K. Bornemann examined the f.p. of mixtures of nickel with

up to 31 per cent. of sulphur, and the results are summarized in Fig. 338. The alleged hemisulphide has no existence under these circumstances, for it has a eutectic structure. Mixtures with over 31 per cent. of sulphur are unstable under atm. press., but K. Bornemann showed that the compounds NiS, Ni_3S_4, and NiS_2 are formed, and they dissociate below the m.p. With mixtures in the range of the diagram, Fig. 337, there are five series of solid soln. which separate from the fused mixtures; the f.p. curve has five branches with eutectic points at 644° and 21·4 per cent. of sulphur, and at 812° with 30·6 per cent. of sulphur. The only compound capable of existence in contact with the molten mixtures is **nickel tritadisulphide,** Ni_3S_2, melting at 787°. H. Fincke, and J. P. Podolsky and N. M. Zarubin obtained it by the action of sulphur on nickel above 600°. According to K. Bornemann, the existence of **nickel hexitapentasulphide,** Ni_6S_5, is probable, but mixtures of this composition lose sulphur when fused. The thermal transformations in the solid state show a well-defined eutectoid at 520°, and 29·7 per cent. of sulphur. K. Bornemann's values for the sp. gr. of the products with *S* per cent. of sulphur were :

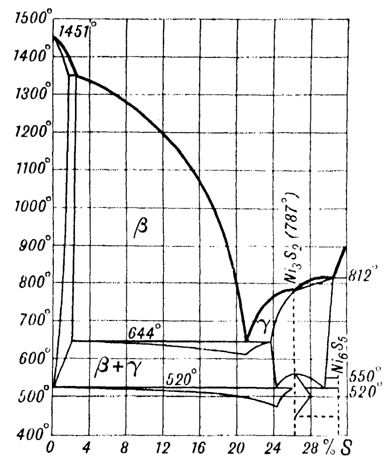

FIG. 338.—The Freezing-point Curves of the System : Ni–S.

S . .	0	5·7	11·5	17·4	21·4	22·3	23·2	24·7
Sp. gr. .	8·86	8·01	7·25	6·62	6·23	6·17	6·09	5·98
S . .	26·2	26·6	27·2	27·9	29·1	29·6	31·0	10
Sp. gr. .	5·87	5·86	5·68	5·71	5·49	5·65	5·50	2·07

W. Guertler studied the ternary system : nickel–sulphur–antimony.

A. G. Werner, and C. A. S. Hofmann described a mineral occurring in acicular crystals in a mine at Johanngeorgenstadt as *Haarkies ;* L. A. Emmerling, R. J. Haüy, and J. F. L. Hausmann regarded this *capillary pyrites* as a variety of iron pyrites until M. H. Klaproth, and D. L. C. Karsten reported that the mineral contained neither iron nor sulphur, but rather nickel associated with arsenic and some cobalt, and in consequence, for a time, the mineral was called *native nickel*—*e.g.*, by W. Haidinger. A. Breithaupt, however, was not satisfied, and said that the nature of the mineral is *unbegreiflich.* J. A. Arfvedson analyzed the mineral and found it to contain 34·26 per cent. of sulphur and 64·35 per cent. of nickel, and the original term was then revived. The term *Haarkies* was modified by F. S. Beudant into *harkise ;* by E. F. Glocker, into *trichopyrite ;* and by E. J. Chapman, into *capillose.* J. F. L. Hausmann called it *Nickelkies* or *nickel pyrites ;* R. Jameson, primatic nickel pyrites, and similar terms were used by F. Mohs, and A. Breithaupt. Varieties were also called *red nickel pyrites,* and *yellow nickel pyrites* by A. Breithaupt ; and P. Groth employed the term *nickel blende.* W. Haidinger applied the term **millerite**—after W. H. Miller—which is the term now employed. It is curious that all this period of uncertainty and confusion should have prevailed for nearly half a century. K. T. Liebe reported a variety from the Lammerichskaule mine in Westerwald, which he called **beyrichite.**

The occurrence of millerite in England, Wales, Scotland, and Ireland has been described by G. A. Kenngott, J. H. Collins, F. J. North and W. E. Howarth, and R. P. Greg and W. G. Lettsom ; in France, by A. Lacroix, and E. Barret ; in Belgium, by A. Firket ; in Portugal, by A. Breithaupt ; in Italy, by G. P. Jervis, D. Lovisato, and A. Scacchi; in Stiermark, by A. Hofmann ; in Bohemia, by V. R. von Zepharovich, G. A. Kenngott, and A. E. Reuss ; in Silesia, by F. Römer, A. von Lasaulx, and H. Traube ; in Saxony, by A. Breithaupt, and A. Frenzel ; in Germany, by H. Laspeyres, G. A. Kenngott, H. Jordan, D. F. Wiser, W. T. Casselmann, E. Weiss, T. Haege, G. Seligmann,

C. L. E. Lottner, P. Groth, M. von Roehl, F. Sandberger, O. Luedecke, C. F. Rammelsberg, and A. Breithaupt; in Canada, by H. How, W. E. Barlow, and G. C. Hoffmann; in the United States, by J. D. Dana, E. L. Fletcher, F. A. Genth, W. P. Blake, W. R. Johnson, and A. V. Leonhard; in Brazil, by P. A. de Sachsen-Coburg-Gotha, and S. Meunier; and in Tasmania, by W. F. Petterd.

Analyses reported by C. F. Rammelsberg, H. Laspeyres, K. T. Liebe, W. von de Marck, F. A. Genth, A. V. Leonhard, and J. A. Arfvedson indicate that millerite is **nickelous sulphide,** NiS, or simply *nickel sulphide;* and this also agrees with the analyses of artificial preparations by H. de Sénarmont, C. F. Rammelsberg, J. L. Proust, and J. L. Lassaigne. K. T. Liebe, and F. W. Clarke regarded beyrichite as an impure nickelosic sulphide, Ni_3S_4, or $2NiS.NiS_2$, but H. Laspeyres showed that beyrichite, from Altenkirchen, like millerite has the composition (Ni,Co,Fe)S; the sp. gr. of beyrichite is rather less than that of millerite, but the crystalline forms are the same. He suggested that millerite is formed from beyrichite by paramorphism.

The preparation of nickel sulphide.—As indicated above, nickel sulphide can be prepared by the direct union of sulphur and nickel; K. Bornemann, and R. Hesse obtained nickel sulphide in this way. R. Tupputi obtained it by the action of sulphur on heated nickel oxide, and also by heating one of the hydrated forms. J. A. Arfvedson prepared the sulphide by passing hydrogen sulphide over red-hot nickel oxide; A. Gautier and L. Hallopeau, by passing an excess of carbon disulphide vapour over red-hot nickel—*vide supra,* nickel hemisulphide; H. de Sénarmont, by heating a mixture of nickel chloride and potassium sulphide; and H. Baubigny, by heating a mixture of nickel sulphate and alkali sulphide in an atm. of hydrogen sulphide; F. Fouqué and M. Lévy, by heating, at 80°, in a sealed tube, a soln. of nickel sulphate with an aq. soln. of hydrogen sulphide saturated in the cold, and containing a little free sulphuric acid; E. Weinschenk by heating a soln. of nickel sulphate with ammonium thiocyanate and acetic acid in a sealed tube at 160°. C. Poulenc obtained it in crystals by heating nickel fluoride to redness in a current of hydrogen sulphide. E. Donath, and G. P. Schweder noted that nickel sulphide is formed when nickel oxide is heated with ferrous sulphide in the presence of some slagging materials, and also in the reduction of nickel sulphate by hydrogen, carbon monoxide, or carbon. E. Glatzel observed that nickel sulphide remains when nickel thiophosphate is heated to a high temp. in the absence of air; C. F. Rammelsberg, when nickel thiosulphate is heated; and, along with nickel sulphate, when nickel hexamminodithionate is heated. R. Lorenz found that nickel sulphide is present in the anode slime when a soln. of potassium chloride is electrolyzed with a nickel anode, and a copper sulphide cathode.

Hydrogen sulphide does not act on soln. of nickel salts which contain free mineral acids, or much free acetic acid, but with neutral soln., **hydrated nickel sulphide** is precipitated. The theory of the action was outlined in **10.** 57, 9. Neutral soln. of nickel salts are slowly acted on by hydrogen sulphide, and all the nickel can be precipitated if sodium acetate be present. The precipitation was found by A. Terreil to vary inversely as the amount of free acid present. Oxalic acid and the oxalates are without effect, since these form insoluble oxalates which hydrogen sulphide does not decompose. Alkali sulphites, hydrogen sulphates, thiosulphates, phosphates, and pyrophosphates, even in slightly acid soln., enable hydrogen sulphide to precipitate the metallic sulphides by double decomposition of the primarily formed nickel salts. According to H. Baubigny, and H. Vestner, the action depends on the acidity of the soln.; on the nature of the acid; on the duration of the action; on the conc. of the hydrogen sulphide in the liquid; and on the temp. G. Bruni and M. Padoa studied the effect of increasing the conc. of the hydrogen sulphide on the soln. of a nickel salt by supplying that agent under pressure in sealed tubes. J. L. R. Morgan and A. H. Gotthelf also showed that as the acidity of the soln. increases, the proportion of the nickel salt precipitated

as sulphide to that remaining in soln. decreases. L. Bruner found that the period of induction—*i.e.* the time required for the appearance of a precipitate in soln. sat. with hydrogen sulphide—increases as the acidity of the soln. increases; and the rate of precipitation of the sulphide decreases as the acidity of the soln. increases. The reaction would be reversible were it not for the existence of other less soluble forms of nickel sulphide. Equilibrium is maintained only when the relations between the precipitated sulphide and the mother-liquid do not change. For if the precipitate becomes very much less soluble, the reaction may proceed virtually to an end so that all the nickel is precipitated. Thus, H. Baubigny found that neutral soln. of nickel salts are completely precipitated in a month's time, not, as J. L. R. Morgan and A. H. Gotthelf supposed, owing to the slowness of the reaction of hydrogen sulphide with the nickel in soln., but rather to the slow removal of the precipitate nickel sulphide from the system as it slowly and irreversibly changes to another insoluble form. The subject was studied by M. M. Haring and B. B. Westfall, A. W. Middleton and A. M. Ward, and O. Ruff and B. Hirsch.

Whilst cobalt and nickel sulphides are not precipitated from acidic solutions by hydrogen sulphide, once the sulphides have been precipitated, they are not so readily soluble in dilute acids. It therefore follows that the sulphide probably undergoes some change into a less soluble form as soon as it has been precipitated. A. Thiel and H. Gessner showed that the sulphide which is precipitated under ordinary analytical conditions consists of a mixture of three forms of nickel sulphide which may be separated more or less completely by $2N$-HCl. The α-form, or **α-nickel sulphide,** readily dissolves in cold $2N$-HCl sat. with hydrogen sulphide; **β-nickel sulphide** dissolves in cold $2N$-HCl only to the extent of 0·033 grm. per litre; and **γ-nickel sulphide** is practically insoluble in $2N$-HCl. On the other hand, the β-form dissolves very readily in boiling $2N$-HCl, whilst the γ-form is only soluble to the extent of about 0·013 grm. per litre. The α- and β-modifications cannot be obtained quite free from the γ-form. A sulphide containing 85 per cent. of the α-form is obtained when dil. soln. of nickel salts are slowly mixed with dil. soln. of alkali metal sulphides at the ordinary temp. and in the absence of air. The β-sulphide, mixed with a little γ-sulphide, is obtained when a solution of nickel acetate, acidified with acetic acid, is precipitated by hydrogen sulphide, or by the precipitation of acetic acidic soln. of nickel salts which contain large quantities of alkali metal tartrates. The γ-form is obtained by boiling the mixed sulphides with $2N$-HCl, or by the precipitation of a hot soln. of a nickel salt acidified with mineral acid. The α-sulphide is stable in the absence of air if kept in contact with pure water. In contact with soln. which dissolve it to a slight extent, it is transformed into a mixture of the β- and γ-forms. This change is effected by $0{\cdot}2N$-acetic acid in the course of a few hours. The β-sulphide is similarly converted into the γ-form if subjected to the action of boiling $2N$-acetic acid for several hours. In the presence of sodium acetate, the action is appreciably retarded. In both cases the transformation of the soluble into the less soluble form depends on the action of a reagent which dissolves the one form and has no appreciable solvent action on the other. The γ-sulphide is crystalline, and the β-form appears to be so, but no evidence has been obtained which would suggest that the α-form is crystalline. The anomalous behaviour of nickel sulphide towards acids is only apparent. Freshly-precipitated nickel sulphide is not insoluble in dil. mineral acids, but in consequence of the presence of the α-form, it dissolves to a considerable extent. Nickel sulphide may be precipitated by hydrogen sulphide from acidic soln., although this reaction is comparatively slow. The precipitated sulphide which is obtained under these conditions is identical with that which remains behind when freshly precipitated nickel sulphide is subjected to the action of acids of the same concentration. The differences of solubility are too great to be explained by colloidal conditions, and must be attributed to polymerization. When nickel sulphide is attacked by acids, apparently well-defined equilibria are reached; but it has not been found possible to approach these equilibria from the opposite side,

from hydrogen sulphide and acid soln. of nickel, even when the corresponding solid sulphide is added to inhibit supersaturation.

Hydrated nickel sulphide is also precipitated from soln. of nickel salts by colourless soln. of ammonium sulphide, $(NH_4)_2S$. The precipitation is not complete if polysulphides are present; and the presence of ammonia was also found by A. Lecrenier to hinder the precipitation. The subject was discussed by A. Lecrenier, A. Villiers, G. Chesneau, F. Stolba, L. Moser and M. Behr, L. L. de Koninck, L. L. de Koninck and M. Ledent; and the inhibition of the precipitation when citrates and tartrates are present, by H. Delffs, and R. Fresenius. According to A. Thiel and H. Ohl, the brown coloration produced by the addition of ammonium sulphide to dil. soln. of nickel salts appears only after an interval. The effect is not due to supersaturation. The velocity of precipitation increases with the conc. of the reacting substances and with the temp. Both ammonia and acids delay the precipitation. It is assumed that the first product of the reaction is the simple α-sulphide, NiS. A precipitate is only produced immediately when the solubility product for this sulphide is exceeded. In other cases the NiS remains in soln., slowly polymerizing to $(NiS)_n$, which is less soluble. The brown liquid is a colloidal soln. In accord with this hypothesis, by precipitating a nickel soln. with an excess of colourless ammonium sulphide and rapidly filtering, a clear soln. may be obtained, which gradually becomes brown. R. Lorenz obtained the sulphide by the electrolysis of a soln. of an alkali salt with a copper cathode and nickel anode. G. Chesneau reported a black precipitate of **nickel polysulphide**, $NiS_{4 \cdot 4}$, to be formed by the action of a soln. of sodium polysulphide, sat. with sulphur, on a soln. of nickel chloride. A soln. of sodium monosulphide dissolves 1·37 grms. Ni per litre; and a soln. of sodium polysulphide, 0·078 grm. per litre.

O. W. Gibbs, and F. J. Faktor observed that when neutral soln. of nickel salts are boiled with a soln. of sodium thiosulphate, nickel sulphide is precipitated, and the action is very rapid in a sealed tube at 120°; and O. Brunck obtained the sulphide as a precipitate from neutral, ammoniacal, or acetic acid soln. of a nickel salt by the addition of sodium hyposulphide. S. M. Kuzmenko, and O. Ruff and B. Hirsch observed that with mixtures of nickel sulphate with zinc, lead, manganous, or cobaltous sulphate in gelatine, the less soluble sulphide tends to be precipitated first by sodium sulphide. E. Beutel and A. Kutzelnigg studied the anodic separation of sulphide films.

C. Winissinger prepared a **colloidal solution** of nickel sulphide by adding a small proportion of a dil. soln. of hydrogen sulphide to a dil. soln. of a nickel salt, and then a few drops of ammonia. The greenish-brown liquor is easily oxidized. A. Müller obtained a colloidal soln. by adding yellow ammonium sulphide to a very dil. aq. soln. of nickel nitrate. The dark brown liquor coagulates in about 24 hrs., but if glycerol be present as a protective colloid, the soln. may be kept a week without flocculation. J. Hausmann used gelatine as protective colloid; and A. Dumansky and A. Buntin, tartaric acid. A. Lottermoser discussed the subject. P. C. L. Thorne and E. W. Pates found that the soln. is coagulated by atm. oxygen; and that the particles are negatively charged. O. F. Tower and E. E. Chapman described the preparation of rhythmic rings of the sulphide. P. B. Ganguly and N. R. Dhar studied the coagulation of the colloidal soln. in light. J. V. Kaspar studied the crystals, and W. Jansen, the fibrous forms of millerite.

The physical properties of nickel sulphide.—Millerite usually occurs in very slender or capillary **crystals,** often in radiating groups sometimes more or less interwoven. It also occurs in columnar tufted coatings, partly globular, and partly radiated. The **colour** is brass-yellow or bronze-yellow, maybe with a grey iridescent coating. The streak is greenish-black; the lustre is metallic; and the fracture uneven. The colour of the artificial sulphide varies from a dark grey to a brass-yellow according to the mode of preparation. According to W. H. Miller, the crystals are trigonal, and have the axial ratio $a:c=1:0·32955$; and H. Laspeyres found that beyrichite crystals have $a:c=1:0·3277$. C. Palache

and H. O. Wood gave for millerite $a : c=1 : 0 \cdot 2183$. According to G. R. Levi and A. Baroni, α-NiS, precipitated by ammonium sulphide, is amorphous; β-NiS, obtained from soln. acidified with acetic acid, has hexagonal crystals with $a=3 \cdot 42$ A., and $c=5 \cdot 30$ A.; and γ-NiS, obtained from soln. acidified with sulphuric acid, has rhombohedral crystals, with $a=9 \cdot 61$ A., and $c=3 \cdot 15$ A. Twinning of millerite occurs about the (0001)-plane; **cleavages** are associated with the $(10\bar{1}6)$-, $(01\bar{1}6)$-, $(10\bar{1}3)$-, and the $(01\bar{1}3)$-faces. A. C. Hawkins described some twisted crystals of millerite. W. Flörke studied the **microstructure,** and the **corrosion figures.** Nitric acid slowly produces iridescent stains on polished surfaces of pentlandite and millerite; and a soln. of mercuric chloride produces a brown stain in places on millerite but not on pentlandite. H. Schneiderhöhn, and M. N. Short and E. V. Shannon noted the general inertness of polished sections to etching liquids—*e.g.* hydrochloric acid, potassium cyanide, ferric chloride, and potash lye. Observations on the crystals were made by V. Goldschmidt and R. Schröder, G. A. Kenngott, H. Laspeyres, T. Haege, G. Seligmann, A. Breithaupt, J. V. Kasper, P. A. de Sachsen-Coburg-Gotha, A. Johnsen, and C. Palache and H. O. Wood. H. W. V. Willems found that the **X-radiograms** correspond with ditrigonal dipyramids. The elementary rhombohedron has the parameter $a=5 \cdot 64$ A., and $\alpha=116° \ 35'$, and it contains 3 mols. N. H. Kolkmeijer, N. H. Kolkmeijer and A. L. T. Moesveld obtained similar results. One sulphur atom is surrounded by three nickel atoms at a distance 2·23 A., two nickel atoms at a distance 2·43 A., and one nickel atom at a distance 3·45 A. W. F. de Jong and H. W. V. Willems, and N. Alsén gave $a=3 \cdot 42$ A., $c=5 \cdot 30$ A., and $a : c=1 : 1 \cdot 55$ and $\alpha=116° \ 36'$ for artificial nickel sulphide. H. Ott gave $a=9 \cdot 61$ A., and $c=3 \cdot 155$ A., and $a=5 \cdot 647$ A., and $\alpha=116° \ 38'$; J. C. Röhner, $a=5 \cdot 612$ A., and $\alpha=116° \ 36 \cdot 2'$; and W. Jansen, $a=5 \cdot 65$ A., and $\alpha=116 \cdot 6°$ for the rhombohedral forms and $a=9 \cdot 60$ A., and $c=3 \cdot 15$ A. for the hexagonal form.

G. A. Kenngott gave 4·601 for the **specific gravity** of millerite from Joachimsthal, but this is too low as a representative value; C. F. Rammelsberg gave 5·65; W. H. Miller, and J. Beckenkamp, 5·26 to 5·30; K. T. Liebe, 5·3 to 5·9; A. Breithaupt, 5·65; and A. V. Leonhard, 5·028. The value 5·25 was calculated by H. W. V. Willems for millerite from the X-radiogram data; N. H. Kolkmeijer and A. L. T. Moesveld calculated 5·348 at 18°; J. C. Röhner gave 5·34 at 30°/4°, and calculated 5·43; and 5·61, by W. F. de Jong and H. W. V. Willems for artificial sulphide. K. T. Liebe gave 4·7 for the sp. gr. of beyrichite, and H. Laspeyres, 4·699. J. J. Saslawsky discussed the mol. vol. W. H. Miller found the **hardness** of millerite to be 3·0 to 3·5. A. Reis and L. Zimmermann studied the subject. H. V. Regnault gave 0·12813 for the **specific heat** of pure nickel sulphide between 15° and 98°; W. A. Tilden gave 0·0972 between −180° and 15°; 0·1248 between 15° and 100°; and 0·1338 between 15° and 324°—the corresponding **molecular heats** are respectively 8·82, 11·33, and 12·14. The subject was discussed by I. Maydel. W. Biltz gave 797° for the **melting point** of nickel sulphide, and found that it is not influenced by a small loss of sulphur. K. Friedrich gave 790° for the m.p. of the tritadisulphide, and he observed a transformation point at 545°. J. Thomsen gave for the **heat of formation** $(Ni,S,nH_2O)=17 \cdot 39$ Cals., and also 19·37 Cals.; $(Ni(OH)_2,H_2S,Aq.)=18 \cdot 63$ Cals.; and $(Ni(NO_3)_2,H_2S,Aq.) = -4 \cdot 9$ Cals. W. Herz studied the **entropy**; and G. Beck, the **free energy.**

A. de Gramont discussed the **spark spectrum** of millerite; A. Mickwitz, and H. G. Howell and G. D. Rochester, the **adsorption spectrum**; and O. Stelling, J. Shearer, and O. Lundquist, the **X-ray spectrum.** R. Robl observed no luminescence in **ultra-violet light**; A. Karl studied the triboluminescence; and W. Herz, the **vibration frequency.** K. Fischbeck and E. Einecke studied the **electrolytic reduction** of the sulphide. F. Beijerinck, and R. D. Harvey found the **electrical conductivity** of millerite to be good. W. Meissner and co-workers studied the resistance at very low temp. F. Streintz measured the electrical conductivity of the compressed powder. T. W. Case observed that the

electrical resistance of millerite is not perceptibly influenced by exposure to light. S. Veil studied the **magnetic properties,** and W. Klemm and W. Schüth found the magnetic susceptibility to be $\chi \times 10^6 = 276$ at $-191°$; 244 at $-78°$; 248 at 20°; 220 at 220°; and 230 at 410°.

The chemical properties of nickel sulphide.—G. F. Hüttig and R. Juza found that the vap. press. of **argon** is lowered by nickel sulphide. According to H. Laspeyres, no sulphur is given off when millerite is heated in a closed tube, and K. T. Liebe's statement that beyrichite does do so is attributed by H. Laspeyres to the presence of polydymite in the specimen employed. A. Mourlot said that the sulphide is reduced in the electric arc furnace. N. Parravano and G. Malquori found the dissociation press. at 600° to be log P_{S_2}. J. A. Arfvedson, and H. Rose found that nickel sulphide is not reduced by **hydrogen** at a red-heat; but I. and L. Bellucci showed that crystalline or amorphous, anhydrous, or hydrated nickel sulphide is easily reduced when heated with hydrogen. S. Miyamoto also noted the reduction of the sulphide by hydrogen in a silent discharge.

H. Rose observed that when calcined in **air,** nickel sulphide is oxidized to a basic sulphate. G. Pavia said that the oxidation occurs in two stages: first, the formation of oxide and the separation of sulphur, and afterwards, the oxidation of sulphur to sulphuric acid which dissolves some of the oxide. The reactions are said to be accelerated in sunlight. R. Scheuer found that the sulphide prepared by wet processes oxidizes more readily than that prepared by dry processes. S. H. Emmens studied the oxidation of the sulphides. According to P. de Clermont and H. Guiot, when recently-precipitated nickel sulphide is strongly compressed, and then powdered between the fingers, the temp. rises through 35° or 45°, and aq. vapour is disengaged. The rise of temp. is due to the rapid oxidation of the sulphide. P. de Clermont found that freshly-precipitated, well-washed nickel sulphide loses moisture when exposed to air on filter-paper, and in 24 hrs. acquires a green colour owing to the formation of a basic sulphate. When the sulphide is exposed under a layer of water several centimetres in depth, the oxidation proceeds more slowly, extending over months, whilst the relative amounts of the insoluble product and of basic sulphate in the latter are much diminished. Since the sulphide dissolves in the sulphate (though only in the presence of sulphur) to form a stable compound, the oxidation of nickel sulphide is never complete. The formation of the basic sulphate was also observed by R. Tupputi, H. W. F. Wackenroder, and W. Herz. W. Gluud and co-workers showed that in the oxidation of precipitated nickel sulphide, free sulphur, and nickel sulphate, thiosulphate, and polythionate are formed. J. S. Dunn and E. K. Rideal found that the temp. coeff. of the oxidation at 25°, 35°, and 45° are, respectively, 2·0, 4·0, 7·6 with the γ-sulphide, and 5·6, 12·0, and 28·4 with the β-sulphide. Intermediate basic salts are formed, and the reaction is accelerated by soluble vanadium salts so that nickel sulphate is produced without the formation of intermediate basic salts. B. Bogitch studied the roasting of nickel mattes. According to A. Mailfert, **ozone** oxidizes nickel sulphide first to the sulphate, and afterwards to nickelic oxide and sulphur trioxide.

H. V. Regnault observed that when heated to redness in **water** vapour, nickel sulphide loses very little sulphur. O. Weigel stated that the solubility of precipitated nickel sulphide in water is 0·000364 per cent., or $16·29 \times 10^{-6}$ mol. per litre at 18°; whilst the solubility of millerite is 0·00048 per cent., or $39·87 \times 10^{-6}$ mol. per litre. L. Moser and M. Behr gave $10^{-9·50}$ for the solubility of nickel sulphide in water, and $1·1 \times 10^{-27}$ for the solubility product. The subject was discussed by I. M. Kolthoff. J. L. R. Morgan and A. H. Gotthelf found the relative solubility products of some sulphides, in mols per litre, in the presence of the S″-ions and the HS′-ions contained in $0·1N$-K_2S, to be Ni, 0·0191; Co, 0·0034; Cu, 0·00021; and Pb, 0·000024. A. Mickwitz observed that with normal sodium sulphide as precipitating agent, a sat. soln. of nickel sulphide contains $0·8 \times 10^{-5}$ per cent. of NiS, and the precipitate is **nickel hydroxyhydrosulphide,** Ni(OH)(HS), and if an excess of hydrogen sulphide is used as precipitant, **nickel hydrosulphide,**

$Ni(HS)_2$, is formed. H. Baubigny also prepared the hydrosulphide. P. de Clermont and J. Frommel found that hot water hydrolyzes the freshly-precipitated sulphide to form hydrogen sulphide and nickel hydroxide.

H. Rose found that nickel sulphide is not attacked by **chlorine** in the cold, but there is a slow action when the sulphide is heated. According to E. Zielinsky, chloridization begins at about 150°. W. Flörke observed that millerite is etched by **bromine** vapour. Millerite is said to be insoluble in **hydrochloric acid.** At first sight, it is rather curious that although cobalt and nickel sulphides are sparingly soluble in cold dilute hydrochloric acid, neither is precipitated in the presence of that reagent by hydrogen sulphide—*vide infra.* R. Tupputi observed that the freshly-precipitated sulphide is attacked very slowly by hydrochloric acid with the evolution of hydrogen sulphide; and O. W. Gibbs said that the precipitate, prepared by the action of a boiling soln. of sodium thiosulphate, is insoluble in boiling hydrochloric and sulphuric acids. W. H. Cone and co-workers found that the rate of dissolution of nickel sulphide in $2N$-HCl is diminished by the presence of hydrogen sulphide, and increased by nascent hydrogen. W. Herz studied the reaction—*vide supra,* for the allotropic forms of nickel sulphide. W. Flörke, and J. Lemberg found that millerite is attacked by a soln. of **sodium hypobromite,** forming some black nickel peroxide.

W. H. Cone and co-workers found that **hydrogen sulphide** is adsorbed more by nickel sulphide than it is by the corresponding sulphides of cadmium, lead, or iron. F. Ephraim found that nickel sulphide is readily soluble in a soln. of **ammonium polysulphide,** but is less soluble in colourless **ammonium sulphide.** P. Berthier observed that moist, freshly-precipitated nickel sulphide dissolves in **sulphurous acid.** E. F. Smith found that millerite is decomposed at 170° by sulphur monochloride; and H. Danneel and F. Schlottmann, that the sulphide is not attacked by **sulphuryl chloride** at ordinary temp., but at 300° to 350°, 8 to 9 per cent. is attacked in an hour. Millerite, and beyrichite are said to be insoluble in **sulphuric acid,** and this is in agreement with O. W. Gibb's observation just indicated. W. Manchot and co-workers studied the complexes formed by **nitric oxide** with nickel sulphide. Millerite, and beyrichite are attacked by **nitric acid,** and by aqua regia, with the separation of some sulphur, and the formation of some sulphuric acid, and of a green soln. of nickel nitrate. G. P. Schweder, and E. Donath found that when millerite is fused with **sodium nitrate,** no nickel is produced, but a nickel matte is formed. H. Rose observed that when the sulphide is heated in a current of phosphine, nickel phosphide and hydrogen sulphide are formed. E. Schürmann found that a soln. of arsenic trioxide has no action on millerite. N. Parravano and G. Malquori studied the reducibility of the sulphide by **carbon**: $2NiS+C=CS_2+2Ni$. G. P. Schweder, and E. Donath said that nickel sulphide at a red-heat is not reduced by powdered carbon, or by **carbon monoxide.** P. de Clermont observed that moist, freshly-precipitated nickel sulphide freely absorbs **carbon dioxide** from the atmosphere. J. Lemberg reported that **hydroferricyanic acid** acts on millerite, forming yellow nickel ferricyanide, and that **hydroferrocyanic acid** produces apple-green nickel ferrocyanide. O. F. Wiede and K. A. Hofmann prepared **nickel triamminothiocarbonate,** $NiCS_3.3NH_3$. B. L. Moldavsky and Z. I. Kumari studied the catalytic action of the sulphide on the hydrogenation of **thiophene.**

G. P. Schweder, and E. Donath observed that nickel sulphide is completely decomposed when it is heated with **copper**: $2Cu+NiS=Cu_2S+Ni$; with an equimolar proportion of **copper oxide,** the reaction may proceed in different ways: $4CuO+3NiS=2Cu_2S+Ni+2NiO+SO_2$; or $4CuO+2NiS=Cu_2S+2Cu+2NiO+SO_2$. B. Garre found that the reaction with **iron** begins at 380°, and there is given off 57 Cals. of heat. E. D. Campbell said that the sulphide cannot diffuse through steel at a bright red-heat. R. Schenck and E. Raub studied the reaction with **nickel oxide**: $NiS+2NiO\rightleftharpoons 3Ni+SO_2$. They observed the formation of γ-solid soln. between Ni_3S_2 and NiS. In the reaction with **nickel sulphate,** $NiS+3NiSO_4$

$=4NiO+4SO_2$, the vap. press. becomes appreciable above 600°, and attains 1 atm. at about 660°. E. F. Anthon observed that precipitated nickel sulphide precipitates sulphides from soln. of **copper sulphate,** and **silver nitrate.** G. Jander and K. Rothschild, and W. Jander and co-workers studied the reaction with **cuprous silicate :** $Cu_2SiO_3+NiS=Cu_2S+NiSiO_3$; and **ferrous silicate.** J. Lemberg found that when millerite is treated with an acidified soln. of **silver sulphate** at 70°, it is coloured violet-blue ; E. Schürmann, that the metathetical reaction with a soln. of **cadmium sulphate** or **lead nitrate** is complete ; with soln. of **zinc sulphate, cobalt nitrate,** or **ferrous sulphate,** incomplete ; and no reaction occurs with soln. of **thallous nitrate.** E. F. Anthon also observed that precipitated nickel sulphide gives precipitates of sulphides from soln. of cadmium sulphate, **lead acetate,** and **ferric chloride.** H. N. Stokes studied the attack by a soln. of ferric chloride. W. Flörke observed that millerite is feebly etched by a soln. of ferric chloride ; and strongly etched by a sulphuric acid soln. of **potassium permanganate.** R. Schenck and E. Raub found that in the ternary system Ni–S–O, nickel reacts rapidly with sulphur dioxide at 550°, but equilibrium is established only after many days, complete conversion into nickel oxide and monosulphide being effected. The equilibrium is univariant, as there are three solid phases, but by removing part of the sulphur dioxide one of these disappears and the equilibrium becomes bivariant. From a consideration of the equilibrium diagram and from measurements of the sulphur dioxide pressure the three phases appear to be nickel oxide, nickel sulphide, and the γ-solid soln. With low pressures of sulphur dioxide the nickel sulphide phase disappears. The reverse reaction with the formation of nickel from nickel oxide and sulphide proceeds only as far as the solid soln. phase below the m.p. (about 1400°) ; bundles of fine hair crystals of the solid phase, or possibly of Ni_3S_2, can be seen throughout the reacting mass in the early stages of this reaction.

G. C. Winkelblech said that the hydrated sulphide, precipitated from soln. of nickel salts by a yellow soln. of ammonium sulphide, contains more sulphur than corresponds with NiS, and it remains black when exposed to air, dissolves sparingly in dil. mineral acids, and is insoluble in acetic acid, and in a soln. of ammonium sulphide. According to H. de Sénarmont, when a soln. of nickel chloride is heated with potassium polysulphide, in a sealed tube at 160°, dark grey **nickelosic sulphide,** Ni_3S_4, is formed. W. F. de Jong and H. W. V. Willems found that the X-ray spectral lines of a sample prepared by H. de Sénarmont's process corresponded with those of NiS_2—*vide* Co_3S_4. G. Natta and L. Passerini found that the sulphide has a cubic lattice of the spinel type, with $a=9{\cdot}41$ A. E. A. Geitner obtained the same compound in rhombohedral crystals by heating nickel with sulphurous acid, or a neutral soln. of sodium sulphite in a sealed tube at 200°. In the latter case nickel oxide first separates out—*vide infra,* polydymite, and sychnodymite. R. Scheuer was unable to prepare nickelic sulphide, Ni_2S_3, and nickel is here contrasted with iron, and cobalt.

L. R. von Fellenberg reported **nickel disulphide,** NiS_2, to be formed by strongly igniting a mixture of nickel oxide, sulphur, and potassium carbonate. The dark iron-grey product is quickly decomposed when heated in chlorine, forming sulphur and nickel chlorides. J. Dewar and H. O. Jones found that a soln. of sulphur in carbon disulphide reacts with nickel carbonyl, forming Ni_2S_3. I. and L. Bellucci obtained only the double sulphide $K_2S.3NiS$, and W. F. de Jong and H. W. V. Willems prepared the disulphides by heating nickel sulphide with sulphur for 30 to 40 hrs. at 170°, and washing the product with carbon disulphide to remove free sulphur. The X-radiograms of the grey powder have established the existence of the disulphide as a chemical individual. The cubic lattice is of the pyrite type with $a=5{\cdot}74$ A. ; the Ni-S atoms are 2·42 A. apart ; and the sp. gr. is 4·31. L. Pauling and M. L. Huggins, J. W. Gruner, and P. Niggli discussed the subject—*vide infra,* bravoite, and henglemite. G. Kalb and E. Meyer discussed the minerals $(Ni,Co)S_2$. According to U. Antony and G. Magri, when

hydrogen sulphide or ammonium polysulphide is added to an ammoniacal soln. of nickel acetate in quantity insufficient to precipitate all the nickel as sulphide, the precipitate obtained has the composition NiS. H. Haraldsen and W. Klemm discussed the magnetic behaviour. When, however, an excess of ammonium polysulphide is added to an ammoniacal nickel soln., the precipitate formed is of very variable composition, but the dark liquid always contains **nickel tetrasulphide,** NiS_4. This sulphide, which is obtained as a black powder, is only slightly attacked by hydrochloric acid, but it reacts vigorously with nitric acid, sulphur being liberated. In an atm. of carbon dioxide, it loses sulphur at 300°, being converted into nickel sulphide, whilst when heated in water in presence of air it slowly oxidizes, giving nickel sulphate and sulphuric acid. Hydrogen sulphide soln. has no action on it, but it is dissolved by a soln. of sulphur or ammonium polysulphides giving a brown liquid. With ammonia soln., it yields an azure-blue liquid containing nickel, but all the sulphur is deposited in a very fine state of division. Measurements of the electrical conductivity of soln. of nickel tetrasulphide in ammonium sulphide show that the nickel salt is present in a colloidal state.

F. Ephraim [2] observed that when nickel sulphate is allowed to act on a soln. of ammonium polysulphide in an air-tight flask for some days, a black crystalline substance—**ammonium nickel sulphide**—with a composition between NH_4NiS_5 and a higher sulphide is formed; but not so with salts of zinc, cadmium, manganese, iron, and cobalt. According to R. Schneider, if hydrated nickel sulphate be melted with nine times its weight each of potassium carbonate and sulphur, and kept at a red-heat for 8 to 10 mins.; the cold product washed with air-free water, and then with absolute alcohol; and the crystals finally dried by press. between bibulous paper and in vacuo over sulphuric acid, or in a current of dry carbon monoxide—there remain crystals of **potassium nickel tetrasulphide,** $K_2S.3NiS$, or $K_2S.Ni_2S.NiS_2$, or $K_2Ni_3S_4$. If less than the above proportion of potassium carbonate and sulphur be employed, some crystals of nickel hemisulphide are formed. The six-sided plates are pale bronze-yellow, but they may become bronze-brown through oxidation or the loss of potassium sulphide. I. and L. Bellucci also prepared the tetrasulphide. R. Schneider found that the salt is unstable in air or water, and it breaks up in accord with the equation: $K_2S.3NiS+H_2=H_2S+K_2S+Ni_2S+NiS$, when it is heated in hydrogen; I. and L. Bellucci could not verify this result, and found the product depends on the time of heating and temp. Metallic nickel is a product of the reaction. J. Milbauer obtained **potassium nickel decasulphide,** $K_2Ni_{11}S_{10}$, by fusing for half an hour, at a red-heat, a mixture of nickel oxide with five times its weight of ammonia thiocyanate, washing the cold product successively with water and alcohol, and drying at 100°. The dark green crystals have a metallic lustre. Hydrofluoric acid acts on the crystals only when warm; hydrochloric acts slowly on the salt; sulphuric acid acts only when warm; aqua regia acts slowly in the cold; the salt is changed when warmed with ammonium sulphide; organic acids, alkali lye, and a soln. of potassium cyanide, copper sulphate, or silver nitrate have no action.

R. Schneider prepared **sodium nickel tetrasulphide,** $Na_2S.3NiS$, by fusing nickel sulphate with six times its weight each of sodium carbonate and sulphur as in the case of the corresponding potassium salt. The sodium salt is rather darker in colour than the potassium salt. K. Friedrich observed that in the Ni_2S–Na_2S system, Fig. 340, the eutectic occurs at 615° with 82 per cent. Ni_2S, and no compounds are formed; similarly also with the system Ni_3S_2, Fig. 339, which has a eutectic at 645° and 84 per cent. of Ni_3S_2. H. Brunner also prepared the double salt.

W. Guertler made a partial study of the system Cu–Ni–S, but there was no evidence of the formation of a **copper nickel sulphide.** A. Stansfield and W. V. Faith studied the constitution of copper-nickel mattes. I. and L. Bellucci obtained by fusing at a high temp. a mixture of a nickel salt with sulphur and

barium oxide, **barium nickel pentasulphide,** BaS.4NiS. M. Houdard heated a mixture of nickel and aluminium in a current of hydrogen sulphide, and after treating the product with water, obtained red crystalline spangles which gradually became black, but no definite **aluminium nickel sulphide** could be isolated.

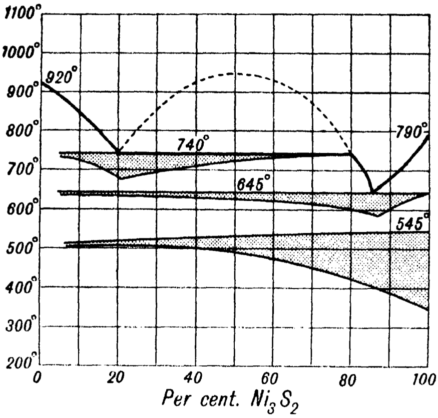

FIG. 339.—The Binary System : Na_2S–Ni_3S_2.

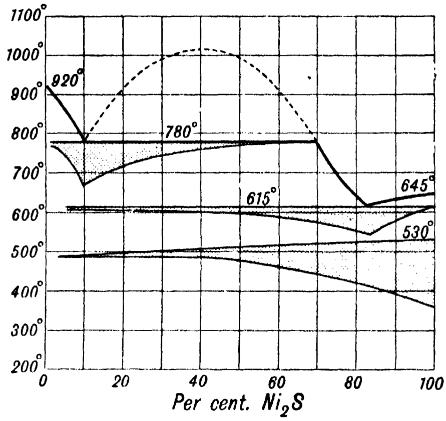

FIG. 340.—The Binary System : Na_2S–Ni_2S.

W. Guertler, and W. Guertler and H. Schack studied the binary system Ni–PbS, and the results are summarized in Fig. 341. There is a **lead nickel disulphide,** $Ni_3Pb_2S_2$, melting at 790°, produced. The same compound appears in the system Ni_3S_2–Pb, Fig. 342, but not in the system PbS–Ni_3S_2, Fig. 343. They also made an incomplete study of the ternary system : Ni–Pb–S. O. Ruff and B. Hirsch studied the subject. G. Masing and L. Koch observed that manganese sulphide forms a eutectic with nickel at 1325°, and 3 per cent. of sulphur.

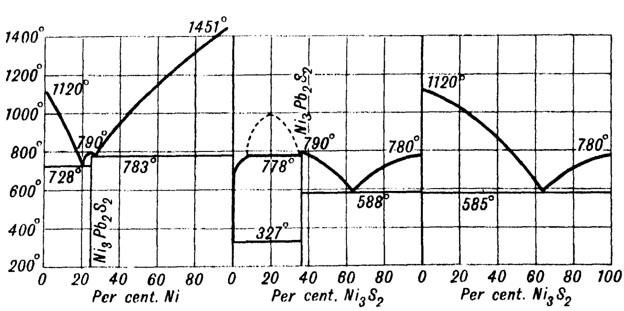

FIG. 341.—The System : Ni–PbS. FIG. 342.—The System : Pb–Ni_3S_2. FIG. 343.—The System : PbS–Ni_3S_2.

J. B. Mackintosh [3] reported crystals of the composition Fe_4Ni_2S in the heart of a shaft furnace smelting roasted nickel pyrrhotite; and an ore was described by W. F. Hillebrand. T. Scheerer obtained a mineral from Lillhammer, Southern Norway, which he found to correspond with an *iron-nickel pyrites,* hence C. V. Shepard called it *nicopyrite ;* whilst A. Weisbach called it *lillhammerite,* after the locality where it was first found. P. A. Dufrénoy had previously suggested the term **pentlandite**—after Mr. Pentland—and this is now the generally accepted name. Analyses of the mineral were reported by T. Scheerer, J. D. Dana, J. H. L. Vogt, D. Forbes, S. L. Penfield, C. W. Dickson, R. Stören, F. W. Clarke and C. Catlett, W. F. Hillebrand, H. Laspeyres, P. Groth, T. L. Walker, and S. H. Emmens. T. Scheerer regarded the mineral as a **ferrous nickel sulphide,** 2FeS.NiS. C. F. Rammelsberg considered it to be an isomorphous mixture of the

two sulphides, (Ni,Fe)S. T. L. Walker, and C. W. Dickson gave the formula (Ni,Fe)$_{11}$S$_{10}$.

Pentlandite has been reported in Norway by T. Scheerer, and J. H. L. Vogt; in Sweden, by J. H. L. Vogt, and G. Landström; in Scotland, by M. F. Heddle, D. Forbes, J. G. Goodchild, and R. P. Greg and W. P. Lettsom; in Cornwall, England, by R. P. Greg and W. P. Lettsom; in Saxony, by E. Geinitz; in Sesia, Italy, by J. H. L. Vogt, G. Tschermek, A. Stelzner, and A. Badoureau; in Sudbury, Canada, by S. L. Penfield, J. D. Dana, C. W. Dickson, T. L. Walker, and S. H. Emmens; in the south-east of Alaska, by by A. F. Buddington; in South Australia, by H. Y. L. Brown; and in Tasmania, by W. F. Petterd.

A number of related minerals has been reported. Thus, J. D. and E. S. Dana, and S. H. Emmens' analyses led them to suggest that one variety of nickel-iron sulphide be called **blueite**; and another variety **whartonite,** but S. L. Penfield showed that both forms are nickeliferous pyrites. The **folgerite** of S. H. Emmens, obtained near Sudbury, Canada, was shown by S. L. Penfield to be only pentlandite. A nickel-iron sulphide obtained by W. F. Petterd from Heazlewood, Tasmania, and called **heazlewoodite,** is related to pentlandite; and similarly also with the **gunnarite** reported by G. Landström to occur in Ruda, Sweden; and the **inverarite** reported by M. F. Heddle to occur near Inverary, Scotland.

W. H. Newhouse studied the system pyrrhotite-pentlandite, or FeS(S)$_n$–(Fe,Ni)S, and the results are summarized in Fig. 344. Pyrrhotite may dissolve up to 13 per cent. of nickel in solid soln. When more than this proportion of nickel is present, the solid soln. breaks down into pyrrhotite and pentlandite when the temp. approaches 600°. Mixtures with over 15 per cent. of nickel are immiscible liquids at the f.p. of pyrrhotite. The crystals of pyrrhotite with nickel in solid soln. are surrounded by liquid pentlandite until about 870°, when pentlandite begins to crystallize in solid soln. with pyrrhotite; as the temp. falls to about 600°, the solid soln. breaks up to form lenticular masses of pentlandite within and along the borders of the crystals of pyrrhotite. These artificial crystals closely resemble those of the natural crystals, and in consequence, the natural crystals of this type are supposed to be formed by the breaking down of an unstable solid soln.

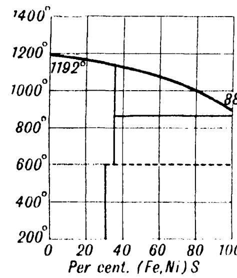

FIG. 344.—Equilibrium Diagram of Pyrrhotite and Pentlandite.

K. Bornemann's observations on the binary system: Ni–Ni$_3$S$_2$, of Ni–S, are summarized in Fig. 346, and his observations on the binary system FeS–Ni$_3$S$_2$, in Fig. 345. There is a compound **ferrous nickel tetrasulphide,** 2FeS.Ni$_3$S$_2$,

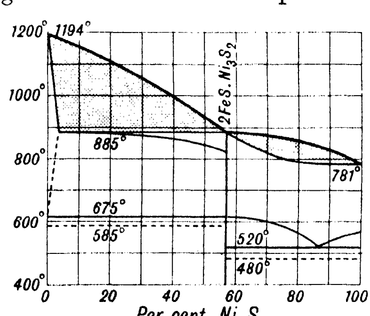

FIG. 345.—The Binary System: FeS–Ni$_3$S$_2$.

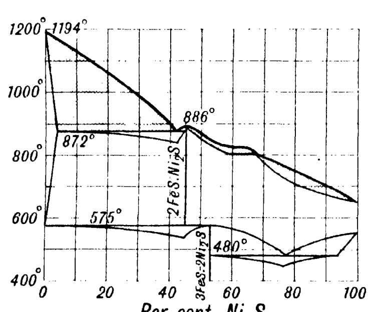

FIG. 346.—The Binary System: FeS–Ni$_2$S.

which melts at 840°, and dissociates considerably when melted. The compound forms solid soln. in all proportions with Ni$_3$S$_2$, but ferrous sulphide dissolves only a very small proportion when in the solid state. There is a number of transformations at lower temp. An examination of the system: Ni$_2$S–FeS, Fig. 346, shows that although nickel hemisulphide is incapable of a separate existence, yet

it forms stable compounds with ferrous sulphide. When in contact with the fused mass, the only stable compound is **ferrous nickel trisulphide,** $2FeS.Ni_2S$, which melts at 886°, and breaks up on cooling to 575°, forming ferrous sulphide and **ferrous nickel pentasulphide,** $3FeS.2Ni_2S$; and at a still lower temp. there is another exothermal change resulting in the formation of $4FeS.Ni_2S$. W. Guertler and W. Savelsberg also confirmed the existence of $2FeS.Ni_3S_2$ and of $2FeS.Ni_2S$.

W. Tonn, and R. Vogel and W. Tonn made a partial study of the ternary system: Fe–Ni–S, or rather of the quaternary system: Fe–Ni–Ni_3S_2–FeS, and some of their results are summarized in Figs. 345 and 347. At ordinary temp. the system has five fields: (i) $A'D'P'_2$ refers to the system containing ferrous sulphide and solid soln. of iron and nickel; (ii) $D'P'_2V'$, ferrous sulphide, $2FeS.Ni_3S_2$, and iron-nickel solid soln.; (iii) $P'_2V'P'_3$, $2FeS.Ni_3S_2$, and iron-nickel solid soln.; (iv) $P_3'C'V'$, $2FeS.Ni_3S_2$, Ni_3S_2, and iron-nickel solid soln.; and (v) $P'_3C'B'$, Ni_3S_2, and iron-nickel solid soln. E_1 refers to the eutectic in the iron-ferrous sulphide system, and S' refers to the critical change at 1407°; V' refers to the critical point in the system: FeS–Ni_3S_2, corresponding with the compound $2FeS.Ni_3S_2$; and E_4, to the eutectoid at 520° in the same system; E_3 refers to the eutectoid 535° in the system: Ni–Ni_3S_2, and E_2 to the eutectic 675°, and W' is the limit of the solidus curve at 645°. At the junctions of the eutectic curves O' is at 825°; G', at 825°; and H', at 585°. If at P_2' the m.p. is 585°; at P_3', 480°; and at S', 1407°. In the region $A'D'C'B'$, only three, viz. binary iron-nickel solid soln., either in the α- or γ-crystal phase according to the composition, FeS; and ternary solid soln. of Ni_3S_2 in $(FeS)_2,Ni_3S_2$ with excess nickel and iron. The metal solid soln. forms eutectics with both sulphide phases. There is a ternary transformation point at 825° at which the liquid containing 38 per cent. Fe, 35 per cent. Ni, and 27 per cent. S, reacts with FeS to form a ternary solid soln. with 39 per cent. Fe, and 32 per cent. Ni, and 29 per cent. S, and a binary solid soln. with 64 per cent. Fe and 36 per cent. Ni. Solid soln. rich in nickel and sulphur decompose at 480°, forming a ternary eutectoid containing 13 per cent. Fe, 27 per cent. S, and 60 per cent. Ni, and consisting of Ni_3S_2, $(FeS)_2,Ni_3S_2$, and nickel-iron solid soln. with 34 per cent. Fe. Ferrous sulphide reacts at 585° with the mixture containing 26 per cent. Fe, 46 per cent. Ni, and 28 per cent. S to form α-$(FeS)_2.Ni_3S_2$, and an iron-nickel solid soln. with 57 per cent. Fe. These results show the nature of the so-called **nickel matte** and explain the presence therein of free metal similar to the hair-copper found in copper matte. This free metal occurs as leaflets when it has separated directly from the liquid mass and in hair-like crystals when it has been formed by the decomposition of ternary solid soln. The subject was studied by A. Stansfield and W. V. Faith.

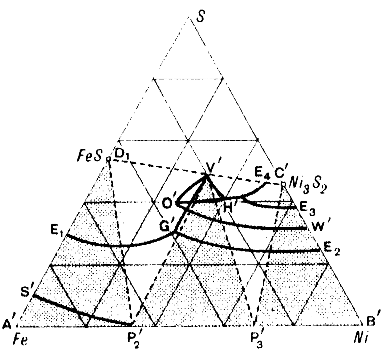

FIG. 347.—The Ternary System: Fe–Ni–S.

Pentlandite is pale bronze-yellow and opaque, with a metallic lustre, and a light bronze-brown streak. Unlike millerite, which is anisotropic, pentlandite is isotropic. Pentlandite belongs to the cubic system, and, according to T. Scheerer, and J. H. L. Vogt, its cleavage is octahedral, and cubic. It occurs massive or in granular aggregates. The crystals were examined by H. Ehrenberg, and J. W. Grimer. N. Alsén examined the X-radiograms and found that the cubic mineral has a=10·02 A.; and after calcination it becomes trigonal with a=3·408 A., and c=5·434 A., so that the axial ratio is $a:c$=1 : 1·549; the artificial mineral has a=3·408 A., and c=5·540 A., or $a:c$=1 : 626. Each Fe and Ni atom has four neighbouring S-atoms at a distance of 2·17 A. W. H. Newhouse also examined

the X-radiograms; and R. D. Harvey, the electrical conductivity. T. Scheerer gave 4·6 for the sp. gr.; S. H. Emmens, 4·73; D. Forbes, 4·5 to 4·6; and S. L. Penfield, 4·946 to 5·006. The value calculated from the lattice data by N. Alsén is 4·93. The hardness of pentlandite is 3·5 to 4·0. It is easily scratched by a needle; millerite is scratched with difficulty. J. Joly gave 480° for the m.p. It is non-magnetic, and, according to F. Beijerinck, a non-conductor of electricity. E. T. Wherry found pentlandite to be a poor radiodetector. The mineral is soluble in nitric acid. F. Carmichael studied the oxidation of the mineral by air and water. H. Schneiderhöhn, and M. N. Short and E. V. Shannon observed the general inertness of the mineral to etching liquids—*e.g.* hydrochloric acid, potassium cyanide, ferric chloride, potash lye, and mercuric chloride. The etching of polished sections of the mineral was discussed by W. M. Davy and C. M. Farnham, and J. Murdock.

J. C. Ullmann [4] described a mineral from Westphalia, and the Grüneau mine near Schutzbach, and called it *weisses Speiskobalt,* and F. von Kobell showed that it was a new mineral, which he called *Nickelwismuthglanz,* and later *saynite,* after the locality Sayn-Altenkirchen; J. Nicol called it grünanite, and A. Breithaupt, *theophrastite.* H. Laspeyres called it **polydymite** from πολύς, many; δίδυμος, twins—in allusion to the polysynthetic twinned forms.

The occurrence of the mineral in the Rhine provinces was discussed by R. Hundt, H. Laspeyres, A. L. Sack, A. Eichler and co-workers, F. von Kobell, C. F. Rammelsberg, etc.; at Sudbury, Canada, by F. W. Clarke and C. Catlett, W. F. Hillebrand, and J. H. L. Vogt; and south-east of Alaska, by A. F. Buddington. Analyses made by F. von Kobell corresponded with $Bi_2S_3.12(Ni,Co,Fe)_2S_3$, and from later work he favoured $Bi_2S_3.R_2S_3$; M. L. Frankenheim favoured $NiS.(Ni,Bi)_2S_3$; and C. F. Rammelsberg, $(Bi,Ni,Co,Fe)_2S_3.(Bi,Ni,Co,Fe)S$, or R_3S_4. H. Laspeyres showed that bismuth is not a necessary constituent, but is present as an impurity in the form of bismuthinite, and he favoured the formula $(Ni,Co,Fe)_4S_5$, analogous with $(Cu,Ni,Co,Fe)_4S_5$, for sychnodymite. F. W. Clarke and C. Catlett's results correspond with Ni_3FeS_5, or R_4S_5. F. Zambonini, and E. T. Wherry and W. F. Foshag reviewed the analyses, and gave Ni_3S_4, **nickelosic sulphide,** and this is in agreement with the observations of M. N. Short and E. V. Shannon. Polydymite is thus considered to be the end-member of the isomorphous series, $(Ni,Co,Fe)_3S_4$, free from cobalt and iron; just as linnæite, Co_3S_4, is considered as another end-member free from nickel and iron. The corresponding terminal member of the triangular $(Fe,Co,Ni)_3S_4$-series, namely, Fe_3S_4, has not been reported.

The opaque mineral may be white with a tinge of yellow, but it is usually silver-grey, passing into steel-grey as the proportion of contained cobalt increases. The mineral occurs compact, and also in octahedral or tabular crystals belonging to the cubic system. Polysynthetic twinning occurs about the (111)-plane. The cubic cleavage is not well-developed. G. Menzer found that the X-radiograms of polydymite, sychnodymite, and linneite are almost identical, and correspond with a face-centred cubic cell with eight Ni_3S_4-molecules per unit cell. The cell is very like that of magnetite. The parameter a=9·405 A.; W. F. de Jong gave a=9·65 A. W. Witteborg also studied the crystals. F. von Kobell gave 5·14 for the sp. gr. of an impure variety; F. W. Clarke and C. Catlett, 4·54; and H. Laspeyres, 4·82. The hardness is between 4 and 5, and the mineral is readily scratched by a needle. A. de Gramont studied the spark spectrum. F. Beijerinck observed that it is a good conductor of electricity. T. W. Case observed that exposure to light had no effect on the electrical resistance. E. T. Wherry found polydymite to be a fair radio-detector. M. N. Short and E. V. Shannon found that with the etching tests nitric acid produces a slight effervescence and darkens the mineral; hydrochloric acid darkens in colour; and negative results were obtained with soln. of potassium cyanide, and mercuric chloride, and potash lye. F. Carmichael studied the oxidation of the mineral by air and water.

The polydymite from the Key West mine in Nevada, and the Vermilion mine

in Ontario differs from the polydymite of Westphalia in some respects. W. Lindgren and W. M. Davy named it **violarite**—from *violaris*, violet—an allusion to the violet-grey colour on polished surfaces of the mineral in vertically reflected light. The violet colour, however, is not considered by M. N. Short and E. V. Shannon to be a general characteristic. Its composition approximates Ni_3FeS_5, and if the iron be deducted as admixed pentlandite, there remains NiS_2. A. F. Buddington observed its probable occurrence in the nickeliferous pyrrotite deposits of South-Eastern Alaska. Violarite occurs as nodules and irregularly-shaped areas in chalcopyrites; and, surrounding the violarite areas, there are zones of millerite. The boundary between the millerite and chalcopyrite is sharp and definite, whilst that between millerite and violarite is hazy and irregular. M. N. Short and E. V. Shannon observed that violarite is isotropic in polarized light, but in some specimens, the areas between the isometric cleavage cracks appear as small interlocking grains of weak anisotropism and diverse optical orientation. In the etching tests on the polished mineral, there is a slow effervescence with nitric acid with the production of brown to black stains; hydrochloric acid is coloured yellow or green; but negative results were obtained with soln. of potassium cyanide, ferric chloride, and mercuric chloride, and with potash lye. F. W. Clarke and C. Catlett concluded that the mineral is identical with polydymite when any allowance is made for the presence of chalcopyrite. M. N. Short and E. V. Shannon found that the mineral approximates $FeS.Ni_2S_3$, or $(Fe,Ni)_3S_4$, and it is thus a member of the $(Co,Fe,Ni)_3S_4$-family. They also showed that the mineral from Julian, California, is the same as violarite from the Vermilion mine, Ontario, in spite of its lacking the violet colour.

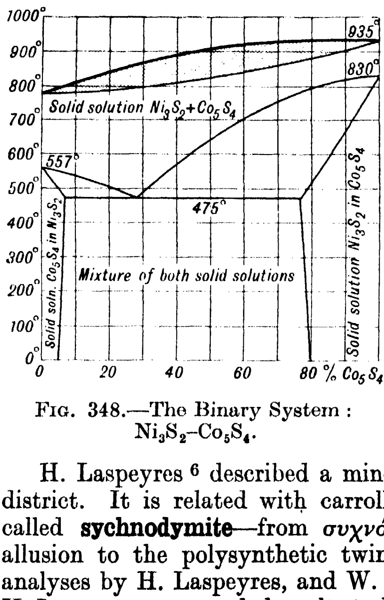

FIG. 348.—The Binary System: Ni_3S_2–Co_5S_4.

W. Guertler [5] and co-workers studied the system: Ni_3S_2–Co_5S_4, and the results are summarized in Fig. 348. There is no evidence of the formation of a **cobalt nickel sulphide.** W. Guertler and H. Schack also made an incomplete study of the ternary system: Co–Ni–S. G. Kalb and E. Meyer studied the occurrence of $(Co,Ni)S_2$; and W. A. Tarr, the linnaeite groups—*vide* **14**. 67, 22.

H. Laspeyres [6] described a mineral from the Kohlenbach mine, in the Siegen district. It is related with carrollite, and with polydymite. The mineral was called **sychnodymite**—from συχνός, crowded, many; and δίδυμος, twins—in allusion to the polysynthetic twinning characteristic also of polydymite. The analyses by H. Laspeyres, and W. Stahl have been represented by $(Co,Ni,Cu)_4S_5$. H. Laspeyres supposed the salts to be derivatives of a cobaltic or a nickelic sulpho-acid $(SH)_2(Co,Ni)$–S–$(Co,Ni)(SH)_2$, but there is no serious evidence in favour of the hypothesis. Analyses were also made by G. Berg, who did not agree with the R_4S_4-formula. F. Zambonini showed that the mineral is better represented by the carrollite formula R_3S_4—both minerals are slightly deficient in sulphur owing, possibly, to the presence of impurities, and to a small loss of sulphur by secondary changes. This is also in harmony with the X-radiograms by G. Menzer, and W. F. de Jong and A. Hoog. With the type formula R_3S_4, H. Laspeyres represented cubanite by $Cu(FeS_2)_2$, and canolite can be regarded as the corresponding cobalt salt $Cu(CoS_2)_2$, and sychnodymite as $(Co,Cu,Ni)_3S_4$, or $(Co,Cu,Ni)\{(Co,Cu,Ni)S_2\}_2$; just as P. Groth and K. Mieleitner considered the series: linnæite, $(Co,Ni,Fe)\{(Co,Ni,Fe)S_2\}_2$; polydymite, $(Ni,Co,Fe)\{(Ni,Co,Fe)S_2\}_2$; carrollite, $Cu(CoS_2)_2$; barracanite $Cu(FeS_2)_2$; and daubréelite, $Fe(CrS_2)_2$. For siegenite, $(Ni,Co,Fe)_3S_4$, with more nickel than cobalt, *vide* cobalt sulphide.

H. Laspeyres found sychnodymite to occur in small, steel-grey octahedral crystals belonging to the cubic system. It also occurs massive. The crystals exhibit polysynthetic twinning about the (111)-plane, analogous with polydymite. G. Menzer found the X-radiograms of sychnodymite, polydymite, and linnæite are almost identical. The elementary cell is a face-centred cube, with the parameter a=9·434 A., and there are eight R_3S_4-molecules in the unit cell. According to H. Laspeyres, the sp. gr. is 4·758. The mineral is insoluble in hydrochloric acid, and forms a red soln. with nitric acid.

W. F. Hillebrand [7] described a mineral from Minaragra, Peru, which is regarded as a highly nickeliferous pyrite, $(Fe,Ni)S_2$, carrying about 4·31 per cent. of vanadium. He called it **bravoite**—after J. J. Bravo. A. F. Buddington observed it in the nickeliferous deposits south-east of Alaska ; and G. Kalb and E. Meyer, at Mechernick, Germany. R. Zückert studied the formation of cobalt-nickel pyrites of Joachimsthal, Bohemia. Bravoite occurs in small grains and crystal fragments, apparently octahedral, and also in pyritohedrons. The colour is pale yellow ; it is whiter than pyrite ; and acquires a faint reddish tarnish on exposure to air. G. Kalb and E. Meyer observed that the crystals from Mechernick have a zonal structure especially apparent on polished surfaces. Zones of a violet-coloured mineral alternate with brass-yellow zones. The boundaries of the zones are parallel with the pyritohedral planes. The composition of both zones approximates $(Fe,Ni)S_2$. W. F. de Jong and H. W. V. Willems observed NiS_2, 53·82 ; CoS_2, 7·12 ; and FeS_2, 39·08 per cent. ; and that this sulphide forms a complete series of solid soln. with the pyrite structure ; and the length of the basal edge of the space-lattice is 5·57 A., the arithmetical mean of the values for the lattices of the two components. G. Kalb and E. Meyer observed that the violet zones have not all the same tinge, and the colour is probably due to the presence of different proportions of nickel and iron. M. N. Short and E. V. Shannon observed no indication of cleavage in this mineral ; its hardness is above 5·5, since it cannot be scratched by a needle. Nitric acid fumes tarnish a polished face of the mineral, and the iridescent stains emphasize the zonal structure. Negative results were obtained with hydrochloric acid, soln. of potassium hydroxide, potassium cyanide, ferric chloride, and mercuric chloride. A. F. Buddington's description of bravoite from Minaragra is the same as that of violarite.

M. Henglein described a mineral from the Victoria mine, Müsen, Westphalia. It was called **hengleinite.** Analyses correspond with the pyritic structure, $(Fe,Ni,Co)S_2$. It occurs as a confused aggregate of cubic crystals, which show the forms of the cube, octahedron, and the pentagonal-dodecahedron. The colour is steel-grey ; the lustre is metallic ; and the streak greyish-black. The cleavage parallel to the faces of the cube is distinct. The sp. gr. is 4·716 at 19° to 20° ; and the hardness, 5·0 to 5·5. When the mineral is heated, it gives off sulphur ; and it is decomposed by nitric acid.

W. R. Schoeller and A. R. Powell [8] reported a mineral from the vicinity of Villamania' Spain, and they called it **villamanite.** The analysis corresponds with $(Cu,Ni,Fe,Co)(S,Se)_2$, so that it belongs to the pyrites family. The mineral contains crystals and radiating fibres so that there are doubts about its homogeneity. E. Thomson considers it to be a mixture and not a mineralogical individual.

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§ 18. Nickel Sulphates

Anhydrous **nickelous sulphate,** $NiSO_4$, or simply *nickel sulphate*, was prepared by J. L. Gay Lussac [1] by heating the hydrated salt to dull redness. A. Étard said that the anhydrous salt is deposited in a crystalline state by evaporating a soln. of the salt in conc. sulphuric acid. P. Klobb, and C. Lepierre and M. Lachaud obtained crystals of the salt by mixing the hydrated sulphate, carbonate, or oxide with an excess of ammonium sulphate, and heating the mixture out of contact with the flame gases, and in a partially closed crucible, until the ammonium sulphate had volatilized. The crystals obtained by the ammonium sulphate process are citron-yellow, or canary-yellow octahedra; and C. Lepierre and M. Lachaud added that if ammonium hydrosulphate is employed, the anhydrous nickel sulphate appears in fusiform, prismatic crystals. The difference in the two forms is due to the presence of about 0·5 per cent. of free sulphuric acid in the fusiform crystals. C. F. Rammelsberg obtained the anhydrous salt by heating hydrated nickel dithionate, or hexamminodithionate when some nickel sulphide may also be formed. F. W. O. de Coninck prepared the anhydrous salt by triturating nickel oxide with sodium hydrosulphate. A. Mailfert noticed that the anhydrous sulphate is formed when nickel sulphide is oxidized by ozonized air.

An aq. soln. of nickel sulphate is obtained by dissolving nickel, the oxide, hydroxide, or carbonate in dil. sulphuric acid; and the evaporation of the aq. soln. at ordinary temp. furnishes crystals of the *heptahydrate*, $NiSO_4.7H_2O$. Analyses of the heptahydrate were made by R. Tupputi, R. Phillips, R. Fulda, E. Mitscherlich, J. C. G. de Marignac, T. Thomson, etc.; the hexahydrate by R. Phillips, J. I. Pierre, E. Mitscherlich, J. C. G. de Marignac, and B. D. Steele and F. M. G. Johnson; and of the anhydrous salt, by R. Tupputi, and P. Berthier. M. J. Fordos and A. Gélis observed that the heptahydrate is formed along with other products when sulphurous acid acts on nickel. A. Terreil recommended the following process for preparing this salt:

Commercial nickel is dissolved in aqua regia, and the soln. evaporated almost to dryness: on treatment of the residue with water, some iron arsenate remains insoluble and is separated by filtration. The copper is precipitated from the soln. by introducing some iron tacks, and the iron in the soln. is peroxidized; then a quantity of sulphuric acid is added sufficient to convert all the iron and nickel present into sulphates, the soln. is evaporated to dryness, and the residue is treated with water, yielding a soln. from which the iron is precipitated by barium carbonate. The filtrate on evaporation deposits crystals of pure nickel sulphate.

D. Weinberger discussed the purification of the salt. Many other processes are available—*e.g.*, H. P. Corson's process. H. Baubigny recommended the following process:

A soln. of nickel nitrate is treated with an ammoniacal soln. of ammonium carbonate and filtered from the precipitated iron oxide. The soln. is boiled to drive off the ammonia, neutralized with sulphuric acid, and the double sulphate is recrystallized a few times. It is then heated to dull redness, and treated with a little water, and soln., acidified with acetic acid, is treated with hydrogen sulphide to remove the copper. The filtrate is mixed with nitric acid, and evaporated to dryness. The product is calcined, dissolved in nitric acid, and the soln. treated with an excess of potassium acetate, and then with sodium nitrite. After standing a few days, the soln. is filtered to remove the precipitated cobalt salt, and the filtrate is treated with hydrochloric acid, and evaporated. The residue is treated with ammonium oxalate. The resulting nickel oxalate is converted into sulphate by treatment with sulphuric acid.

A. Cronstedt noted in 1751 that this salt which he called *nickel-viktril* occurs as a deep green efflorescence on the kupfernickel of the cobalt mines of Helsingland. T. Bergman said: *niccolum vitriolatum interdum e mineris sulphuratis fatiscentibus genitum,* and the term *nickel vitriol* was applied to it during the first half of the nineteenth century. F. von Kobell then termed it *pyromelin;* but D. A. Casares had previously named it *morenosita*—after St. Moreno—and hence it is now called **morenosite.** A. M. Alcibar wrote on the subject.

The occurrence of morenosite in the Rhenish Schiefergebirge was described by H. Laspeyres; in Bayreuth, by F. von Kobell; in Rieschelsdorf, by R. Fulda; in Scotland, by J. G. Goodchild; in Zermatt, Switzerland, by F. Pisani; in Monzaïd, Algeria, by A. Lacroix; in Galicia, Spain, by D. A. Casares; in Joachimastal, Bohemia, by F. Ulrich; in the Wallace mine, Lake Huron, and in the Gap nickel mine, Lancaster Co., Pennsylvania, by J. D. Dana; in the Phœnix mine, Napa Co., California, by G. T. Becker; and in San Miguel, Peru, by A. Raimondi. Analyses were reported by R. Fulda, and F. Pisana.

A number of hydrates have been reported. R. Tupputi observed that at 12·5° one part of hydrated nickel sulphate dissolves in three parts of water; C. von Hauer, that at 11° to 14°, a sat. aq. soln. contained 28·84 per cent. $NiSO_4$, and at 18° to 20°, 30·77 per cent.; C. H. Griffiths, that a sat. soln. at 112·5° has 65 per cent. of $NiSO_4$; and E. Tobler, that 100 grms. of water dissolve 30·4 grms. $NiSO_4$ at 2°; 41 grms. at 23°; 52 grms. at 50°; 57·2 grms. at 60°; and 61·9 grms. at 70°. More exact measurements were made by A. Étard, and by B. D. Steele and F. M. G. Johnson. F. Rüdorff gave for the ice-line 12·7 per cent. of $NiSO_4$ at −1·60°; 17·7 per cent. at −2·95°; and 20·6 per cent. at −4·15°, which is the eutectic temperature. Observations were made by I. Koppel and H. Wetzel, F. Rüdorff, A. Chrétien and R. Rohmer, N. V. Tantzoff, L. Hackspill and A. P. Kieffer, C. Montemartini and L. Losana, R. M. Caven and W. Johnston, G. J. Mulder, A. and H. Benrath, R. Lattey, and F. C. Vilbrandt and J. A. Bender. M. A. Rakuzin and D. A. Brodsky studied the thermal dehydration of the salt. B. D. Steele and F. M. G. Johnson gave for the percentage solubility, *S*, and the solid phases, Fig. 349,

	0°	15°	31·5°	32·3°	53·3°	70°	90°	110°
S . . .	21·4	25·5	30·2	30·4	34·5	37·3	43·3	46·5
	$\underbrace{\qquad}$ $NiSO_4.7H_2O$			$\underbrace{\qquad}$ $NiSO_4.6H_2O$ (blue)		$\underbrace{\qquad}$ $NiSO_4.6H_2O$ (green)		

A. Étard observed that the percentage solubility at 119° is 49·4 per cent., and that there is a probability of a transformation into the dihydrate near this temp. since the solubility decreases to 36·3 per cent. at 163°, and at 230°, is nearly zero. The results are summarized in Fig. 349.

T. Graham said that a pale yellow *monohydrate*, $NiSO_4.H_2O$, remains when a higher hydrate is heated to 103·3°, and that the odd mol. of water persists up to 279·4°. H. Lescœur obtained the monohydrate as a precipitate by adding conc. sulphuric acid to a soln. of nickel sulphate. R. Rohmer observed that both the monohydrate and the anhydrous salt can be prepared at 25° in the presence of sulphuric acid. B. D. Steele and F. M. G. Johnson found that the pale green *dihydrate*, $NiSO_4.2H_2O$, separates from a sat. soln. of nickel sulphate at 131°;

and A. Étard, that the dihydrate is precipitated from a sat. aq. soln. of nickel sulphate by the addition of conc. sulphuric acid. C. A. L. de Bruyn reported a *tetrahydrate*, $NiSO_4.4H_2O$, by recrystallizing nickel sulphate from sulphuric acid of sp. gr. 1·4. The tetrahydrate is metastable, and it was found by R. Rohmer to exist at 25° in contact with soln. with less than 43 per cent. of H_2SO_4. The *pentahydrate*, $NiSO_4.5H_2O$, analogous to pentahydrated ferrous sulphate, has not been prepared, but J. W. Retgers found that there is a narrow range of solid soln. of the pentahydrate with pentahydrated cupric sulphate—*vide infra*. According to J. C. G. de Marignac, and G. N. Wyrouboff, the *hexahydrate*, $NiSO_4.6H_2O$, is dimorphous—one form, the *α-hexahydrate*, occurs in blue, or bluish-green, quadratic or tetragonal crystals, and the other, the *β-hexahydrate*, in green, monoclinic crystals. B. D. Steele and F. M. G. Johnson found the transition temp. to be 53·3°, and the ranges of stability are indicated in Fig. 363. H. J. Brooke, R. Phillips, and J. I. Pierre obtained the blue, tetragonal α-form from soln. containing an excess of acid, say by evaporating, at 15° to 18°, an aq. soln. of the nickel sulphate mixed with half its weight of sulphuric acid; and C. A. L. de Bruyn, sulphuric acid of sp. gr. 1·3 to 1·4. P. Groth gave for the axial ratios $a : c = 1 : 1·912$. C. von Hauer employed conc. hydrochloric in place of sulphuric acid. E. Mitscherlich obtained it from neutral soln. between 15° and 20°; and J. C. G. de Marignac, between 30° and 40°. R. Phillips said that when the heptahydrate is exposed to air, it loses water and forms the hexahydrate; and E. Mitscherlich, that the heptahydrate when placed on paper and exposed to sunlight for 2 or 3 days is converted into an aggregate of quadratic bipyramids. D. Dobroserdoff, however, showed that sunlight has no effect on the heptahydrate provided the crystals are contained in a space saturated with water vapour, and maintained at a low temp. The observed phenomenon is therefore a simple case of efflorescence. The green, monoclinic β-form was obtained by J. C. G. de Marignac by the isothermal crystallization of neutral soln. of nickel sulphate at 50° to 70°; I. Koppel and H. Wetzel said at 53·3°, and B. D. Steele and F. M. G. Johnson, 60° to 70°. J. C. G. de Marignac said that large, stable crystals are obtained from soln. of nickel sulphate containing some nickel chloride and free hydrochloric acid. The crystals should be dried at 40° to 50°. The green, transparent crystals are stable at 40°, but at ordinary temp. they become blue, and opaque. R. Reinicke studied the nature of the hydrates.

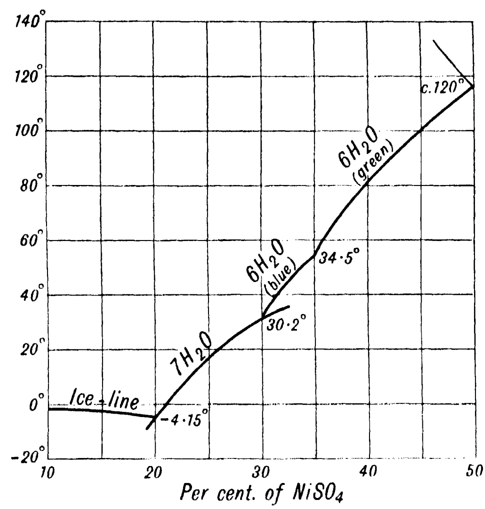


FIG. 349.—The Solubility Curves of Nickelous Sulphate in Water.

The physical properties of nickel sulphate.—Anhydrous nickelous sulphate occurs in citron-yellow or yellowish-green, octahedral **crystals.** The heptahydrate forms emerald-green, rhombic crystals which, according to J. C. G. de Marignac, have the axial ratios $a : b : c = 0·9815 : 1 : 0·5656$; H. G. K. Westenbrink gave $0·9804 : 1 : 0·5631$. R. W. Cairns and E. Ott's X-radiograms showed no evidence of the existence of two crystalline forms of nickel sulphate. C. Winther studied the extinction coeff. of soln. Morenosite occurs in acicular crystals and thin prisms; there are also fibrous forms, and it also occurs as an efflorescence; the colour ranges from apple-green to greenish-white. The streak is white with a

green tinge. The **cleavage** on the (010)-face is complete. L. Royer studied the overgrowths on mica. The **corrosion figures** were found by E. Blasius to resemble those obtained with heptahydrated magnesium sulphate. H. Dufet observed that the crystals are isomorphous with the rhombic crystals of heptahydrated magnesium, and zinc sulphates. A. des Cloizeaux gave for the **optic axial angle** $2E=64°\ 24'$ with red light; and W. von Lang, $2E=64°\ 12'$; whilst H. Dufet gave $2V=41°\ 54'$, and H. Töpsöe and C. Christiansen gave $2V=41°\ 56'$. Observations on the crystals were also made by E. Mitscherlich, C. F. Rammelsberg, L. de Boisbaudran, and C. A. L. de Bruyn. According to E. S. von Federoff, there is a monoclinic modification of the heptahydrate which is obtained in an unstable form by crystallization from a supersaturated soln. of the heptahydrate, and it rapidly changes into the ordinary rhombic form. G. N. Wyrouboff suggested that the heptahydrate may be trimorphous—rhombic, monoclinic, and rhombohedral; and S. Durkacz found that $NiSO_4.nH_2O$, and $CuSO_4.nH_2O$ are isotrimorphous, and furnish the solid soln. with 0 to 10·37 per cent. $NiSO_4.5H_2O$ are triclinic; those with 42·53 to 60·57 per cent. $NiSO_4.7H_2O$ are monoclinic; and those with 93·58 to 100 per cent. $NiSO_4.7H_2O$ are rhombic. E. Dittler studied nickel sulphate associated with manganese and magnesium sulphates. L. C. Jackson, and F. M. Jäger and H. Haga examined the **X-radiograms.** H. G. K. Westenbrink found the lattice dimensions of the heptahydrate to be $a=11·86$ A., $b=1208$ A., and $c=6·81$ A., and there are 4 mols. per cell. C. A. Beevers and C. M. Schwartz inferred that the rhombic form of the heptahydrate has six H_2O-molecules around the Ni-atom, forming an almost regular octahedron. The SO_4-group is tetrahedral. Each SO_4-group is in contact with six Ni-groups; each Ni-group is in contact with SO_4-groups, and also two neighbouring Ni-groups. The seventh water molecule is associated with nickel by two positive bonds. L. C. Jackson's observations on the magnetic susceptibility favoured the assumption that the nickel atoms are arranged on the space-lattice as indicated in Fig. 350. C. A. Beevers and H. Lipson gave for the tetragonal form of the hexahydrate $a=9·61$ A., and $c=18·3$ A. with 4 mols. per unit cell, and tetrahedral SO_4-groups, and octahedral $Ni(6H_2O)$ groups. R. B. Corey and R. W. G. Wyckoff discussed the subject. The blue or bluish-green, tetragonal crystals of the α-hexahydrate, discovered by E. Mitscherlich, were found with the axial ratio $a : c=1 : 1·9061$; A. Scacchi gave $1 : 1·9119$. The (001)-cleavage is perfect, and the (100)-cleavage imperfect. E. Blasius, and H. Baumhauer studied the corrosion figures. The crystals were also examined by H. J. Brooke, J. C. G. de Marignac, F. E. Reusch, P. Groth, C. F. Rammelsberg, and G. N. Wyrouboff. The green or emerald-green monoclinic prisms of the β-hexahydrate, discovered by J. C. G. de Marignac, were found to have the axial ratios $a : b : c=1·3723 : 1 : 1·6763$, and β, $98°\ 17'$. The crystals are also similar to those of the corresponding magnesium salt. A. Scacchi observed no cleavage planes. L. de Boisbaudran examined the effect of inoculating sat. soln. of the hexahydrate with crystals of different kinds; W. E. Garner, the growth of the crystals; and G. Tammann and H. E. von Gronoff, the crystallization of supersaturated soln.

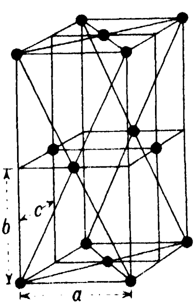


FIG. 350.—Arrangement of the Nickel Atoms on the Space-Lattice of the Heptahydrate.

H. Schröder found that the **specific gravity** of the unfused anhydrous sulphate is 3·652 to 3·696; L. Playfair gave 3·526; T. E. Thorpe and J. I. Watts, 3·418 at 15°, and the mol. vol., 44·6. For the heptahydrate, H. Kopp gave 2·037; H. Schiff, 1·931; E. Moles and M. Crespi, 3·543 at 25°/4°; B. Gossner, 1·953; C. Pape, 1·877 at 16°; O. Pettersson, 1·955 at 14°; E. Moles and M. Crespi, 1·976 at 25°/4°; and T. E. Thorpe and J. I. Watts, 1·947 at 15°, and 144·6 for the mol. vol. H. G. K. Westenbrink calculated 1·882 from the lattice data—observed 1·953.

R. Fulda gave for morenosite 2·004; and E. Günther, 1·937. For the tetragonal α-hexahydrate B. Gossner gave 2·064; H. Töpsöe, 2·074; and T. E. Thorpe and J. I. Watts, 2·031 at 15°; for the monoclinic β-hexahydrate, B. Gossner gave 2·036; and H. Töpsöe, 2·042; and E. Moles and M. Crespi, for the monohydrate, 2·885 at 25°/4°. Observations on the sp. gr. of aq. soln. of nickel sulphate were made by A. Bromer, G. Charpy, G. Dreyer, F. Flöttmann, J. A. Groshans, F. Fouqué, G. T. Gerlach, E. Klein, J. G. MacGregor, L. Mond and R. Nasini, W. W. J. Nicol, and G. Quincke. The general results at 18° are:

$NiSO_4$.	1	4	8	10	14	18 per cent.
Sp. gr. .	1·0091	1·0415	1·0852	1·1085	1·1575	1·2090

The International Critical Tables gave for the effect of temp., the sp. gr. of the soln.:

		0°	18°	20°	25°
Sp. gr.	1 per cent. .	1·0107	1·0091	1·0089	1·0073
	2 ,, .	1·0215	1·0198	1·0196	1·0177
	4 ,, .	1·0435	1·0415	1·0413	1·0389
	6 ,, .	—	1·0630	1·0625	1·0610

W. W. J. Nicol discussed the mol. vol. of aq. soln.; and E. N. Gapon, the mol. vol. of the hydrates. G. Dreyer gave for the temp. of **maximum density** for 0·5, 1·0, and 1·5 per cent. soln., respectively, 3·27°, 2·55°, and 1·83°. J. N. Rakshit found the vol. contraction in the production of $NiSO_4.nH_2O$ with n=1, 6, 7, 60, and 100 to be, respectively, 6·1, 23·6, 26·0, 42·3, and 44·9. P. A. Favre and C. A. Valson found for the volume obtained by dividing the total weight of water and salt by the sp. gr. of soln. with N-gram-equivalents per kgrm. of water, at 23·5°, and the increase in vol. with each successive equivalent of salt:

		N-	$2N$-	$3N$-	$4N$-	$5N$-	$6N$-	$8N$-
$NiSO_4$.	Sp. gr. .	1·079	1·153	1·224	1·292	1·358	1·421	—
	Volume .	999	1002	1007	1014	1022	1031 c.c.	—
	Vol. incr.	1	3	5	7	8	9 c.c.	—
$NiSO_4.7H_2O$	Sp. gr. .	1·073	1·136	1·190	1·238	1·280	1·317	1·378
	Volume .	1062	1127	1194	1262	1330	1400	1541 c.c.
	Vol. incr.	62	65	67	68	68	70	71 c.c.

F. Flöttmann found the sp. gr. of a 1 per cent. soln. at 15°, 20°, and 25° to be respectively 1·0099, 1·0089, and 1·0077. J. N. Rakshit, and E. Moles and M. Crespi discussed the mol. vol. of the water of hydration. S. Oka measured the **surface tension** of soln. G. Tammann studied the **inner pressure** of soln. The **hardness** of the crystals of morenosite is 2·2 on Mohs' scale. The **viscosities** of aq. soln. containing N-, 0·5N-, 0·25N-, and 0·125N-$NiSO_4$, at 25°, observed by J. Wagner, are, respectively, 1·3615, 1·1615, 1·0751, and 1·0323 (water unity). Observations were made by M. Matsui and S. Oguri, who found a break at 31·8° corresponding with the passage from the hepta- to the hexa-hydrate. E. Dittler discussed the **diffusion** of the salt in solid crystals; and J. J. Coleman, aq. soln. C. Pape gave 0·216 for the **specific heat** of the anhydrous sulphate; 0·237, for the monohydrate; and 0·341, for the heptahydrate. H. Kopp gave 0·313 for the sp. ht. of the heptahydrate, and 82·3 for the mol. ht. The subject was discussed by I. Maydel. S. Pagliani gave for the sp. ht., c, of soln. of a mol. of $NiSO_4$ with n mols of H_2O, $c\times10^2=96+18(n-\gamma)$. J. C. G. de Marignac gave for soln. with 50 and 200 mols of water per mol of salt, 0·8371, and 0·9510, respectively. The subject was discussed by J. Perreu, N. de Kolossowsky, and K. Jauch.

B. D. Steele and F. M. G. Johnson found the **eutectic temperature** of the heptahydrate is −4·15°, Fig. 349; and I. Koppel and H. Wetzel gave −3·9°. F. Rüdorff made observations on this subject; B. D. Steele and F. M. G. Johnson found the **transition temperature** for $NiSO_4.7H_2O \rightleftharpoons NiSO_4.6H_2O$ (blue)+sat. soln., to be 31·5°; I. Koppel and H. Wetzel obtained a similar result; N. V. Tantzoff gave 31·55°; and M. Matsui and S. Oguri, 31·8°. B. D. Steele and

F. M. G. Johnson gave for $NiSO_4.6H_2O$ (blue)$\rightleftharpoons NiSO_4.6H_2O$ (green), 53·3°; N. V. Tantzoff gave 36·7° for the transformation from the heptahydrate to the green hexahydrate. According to B. D. Steele and F. M. G. Johnson, the transformation $NiSO_4.6H_2O$ (green)$\rightleftharpoons NiSO_4.2H_2O$+sat. soln., occurs probably between 118° and 131°. According to A. Fock, the rhombic crystals of the heptahydrate, at room temp., pass into the tetragonal hexahydrate at 33°, and into the monoclinic hexahydrate at 60°. W. A. Tilden gave 98° to 100° for the **melting point** of the heptahydrate. The idea that the heptahydrate loses a mol. of water on exposure to sunlight, due to R. Phillips, J. C. G. de Marignac, E. Mitscherlich, and C. von Hauer, was shown by D. Dobroserdoff to be a simple case of efflorescence. F. Krafft found that when the heptahydrate is placed in the vacuum, corresponding with that for the cathode light, 6 mols. of water are lost in 45 hrs., and the seventh mol. is lost at 280°. H. von Blücher found that the anhydrous salt in air absorbs moisture until the hexahydrate is formed. The **dissociation pressure** was studied by G. Wiedemann, M. Copisarow, D. G. R. Bonnell and L. W. Burridge, and H. Debray; and W. T. Müller-Erzbach observed that the vapour pressure of the salt relative to that of water (unity) is 0·65, it then falls to 0·0007 from 0·003, and is imperceptible after 2 months, when a mol. of water has been lost. E. Wiedemann found that when the heptahydrate is heated in a dilatometer, there is a regular expansion from 20° to 65°, and at 65° there is a large expansion attended by the loss of water, the expansion then proceeds regularly up to 95°; on cooling, the contraction proceeds regularly to 30°, and the original hydrate is reproduced. C. von Hauer observed that the salt loses about 4 mols. of water at 100°; T. Graham, that 6 mols. are lost at 103·3°, and the remaining mol. of water at 279·4°; and J. I. Pierre, that the salt gradually becomes greenish-yellow and anhydrous at 200° to 250°. R. Tupputi said that at a still higher temp., the sulphate decomposes, without melting, to form a basic salt, and at a red-heat nearly all the acid is driven off. H. O. Hofman and W. Wanjukoff observed that the decomposition of the anhydrous sulphate commences at about 702°, and proceeds energetically at 764°. A. Ditte found that the decomposition begins at 440°; F. Warlimont, at 600°; and G. Marchal, at 690°. K. Friedrich and A. Blickle observed that the temp. at which the dissociation press. is equal to 1 atm. is 840°, and G. Marchal, 883°. K. Flick said that the salt decomposes at 850° and 760 mm. press. G. Marchal observed the partial press. of sulphur dioxide, P_{SO_2}, sulphur trioxide, P_{SO_3}, and oxygen, P_{O_2}, when the total press. is P mm.:

	700°	740°	780°	820°	860°	900°	945°
P .	12·6	26·5	78·0	195·0	460·0	1030	2200·0
P_{SO_3} .	1·4	2·6	8·5	22·5	56·1	132·4	289·0
P_{SO_2} .	7·4	15·9	46·3	115·0	269·2	598·4	1274·0
P_{O_2} .	3·7	7·9	23·1	57·5	134·6	299·2	636·0

H. H. Willard and R. D. Fowler, L. Wöhler and K. Flick, and K. Flick studied the separation of metals based on differences in the rates of thermal decomposition of their sulphates. I. Bencowitz and H. T. Hotchkiss studied the lowering of the **vapour pressure** of the hexahydrate.

W. Müller-Erzbach found the relative **vapour pressure** of water and the heptahydrate is 0·56, and the difference becomes inappreciable after the salt has lost a mol. of water. H. Lescœur observed that the vap. press. of a sat. aq. soln. is about 14·4 mm. at 20°. W. C. Schumb studied the dissociation press. of the heptahydrate. G. Tammann found that soln. of 11·31, 26·41, and 39·05 grms. of $NiSO_4$ per 100 grms. of water lowered the vap. press. of water at 100°, 7·4, 17·4, and 32·6 mm. respectively; and the lowering of the vap. press., p mm., of soln. with 25 and 45 grms. of $NiSO_4$ in 100 grms. of water, were:

	30°	50°	70°	90°	95°
p {25 . .	1·0	2·8	6·7	13·4	15·5 mm.
p {45 . .	2·5	7·0	16·6	33·2	38·6 ,,

C. Dieterici, and I. Bencowitz discussed the lowering of the vap. press. of soln. The lowering of the **freezing point,** $\theta°$, of water for soln. with C grms. of $NiSO_4$ per 100 grms. of water for $C<0{\cdot}2028$ was measured by H. Hausrath, and for soln. with $C<0{\cdot}743$ grm. by H. C. Jones:

C . .	0·006874	0·04655	0·2028	0·743	2·245	5·975	14·94
$\theta°$ fall .	0·001583°	0·00960°	0·03585°	0·130°	0·320°	0·720°	1·724°

There is a minimum in the curve for the mol. lowering of the f.p. for $0{\cdot}869M$-$NiSO_4$, and with the most conc. soln., it is less than that of water. This is taken to mean that the nickel sulphate is polymerized in such soln. to an extent which masks any ionization which may have occurred. Consequently, the mol. lowering of the f.p. is less than would be produced by the completely non-ionized, and non-polymerized sulphate. Observations on the subject were also made by N. Tarugi and G. Bombardini, L. Royer, and L. Kahlenberg. E. Plake, and L. Kahlenberg also measured the raising of the **boiling point,** $\theta°$, of soln. with C grms. of $NiSO_4$ in 100 grms. of water, and found:

C . .	2·766	11·196	23·143	34·461	37·735
$\theta°$ rise .	0·096°	0·336°	0·738°	1·389°	1·734°

The **heat of formation** of heptahydrated nickel sulphate is, according to J. Thomsen, $(Ni,O_2,SO_2,7H_2O)=162{\cdot}53$ Cals.; $(Ni,O,SO_3,Aq.)=86{\cdot}95$ Cals.; $(Ni,H_2SO_4,Aq.)=18{\cdot}59$ Cals.; and $(Ni(OH)_2,SO_3,Aq.)=26{\cdot}11$ Cals. R. Schenck and E. Raub gave 232 Cals. for the heat of formation $NiSO_4$. The **heat of neutralization** of $\frac{1}{2}Ni(OH)_2$ by $\frac{1}{2}H_2SO_4$ aq. is 12·336 Cals. G. Marchal calculated 62·8 Cals. for the **heat of dissociation** of the sulphate at 800° to 900°. P. A. Favre and C. A. Valson gave for the **heat of solution** of a mol of the heptahydrate in water −3·888 Cals.; and J. Thomsen gave −4·25 Cals. for a mol of the heptahydrate in 800 mols of water, and −2·42 Cals. for a mol of the hexahydrate. J. Perreu, and E. Plake measured the heats of dilution of aq. soln.

The **absorption spectrum** has been previously discussed. J. Angerstein, T. Swensson, W. V. Bhagwat, and Y. Shibata made observations on the subject. H. M. Vernon studied the changes in colour which occur on dilution, and on raising the temp. E. J. Houston also made observations on the **colour** of the aq. soln. H. Hegge, F. Müller, and E. Lohmann studied the extinction coeff.; and M. Padoa and N. Vita, the transparency of the soln. H. Töpsöe and C. Christiansen observed that the blue, tetragonal hexahydrate has the **indices of refraction** $\omega=1{\cdot}5078$ and $\epsilon=1{\cdot}4844$ for the C-line; $\omega=1{\cdot}5109$ and $\epsilon=1{\cdot}4873$ for the D-line; $\omega=1{\cdot}5173$ and $\epsilon=1{\cdot}4930$ for the F-line; and $\omega=1{\cdot}5228$ for the G-line. The birefringence of the green, monoclinic hexahydrate was found by G. N. Wyrouboff to be negative. A. des Cloizeaux found the birefringence of the heptahydrate to be negative. V. von Lang gave for the index of refraction of the heptahydrate, 1·4660, 1·4672, and 1·4700, respectively, for red, yellow, and green light; and H. Töpsöe and C. Christiansen gave $\alpha=1{\cdot}4669$, $\beta=1{\cdot}4888$, and $\gamma=1{\cdot}4921$ for the D-line; and $\alpha=1{\cdot}4729$, $\beta=1{\cdot}4949$, and $\gamma=1{\cdot}4981$ for the F-line; and H. Dufet gave for the D-line $\alpha=1{\cdot}4693$, $\beta=1{\cdot}4893$, and $\gamma=1{\cdot}4928$. F. Flöttmann found the refraction index of a 1 per cent. soln. of nickel sulphate at 15°, 20°, and 25° to be, respectively, 1·33540, 1·33497, and 1·33451. Observations were also made by J. H. Gladstone and W. Hibbert. W. Vethake compared the mol. refraction of soln. of nickel sulphate and of its complex salts with ammonia. E. K. Plyler, O. Lundquist, and M. Ishino and K. Kojima studied the **X-ray spectrum.** L. Longchambon found that the rotation of the plane of polarization of the heptahydrate in the direction of the optic axes is 6·1° for $\lambda=579\mu\mu$. W. König, R. W. Roberts and co-workers, and L. Longchambon studied the magnetic rotatory power. H. C. Jones found that the refractive indices, μ, of soln. with C mols of nickel sulphate per litre increase regularly with concentra-

tion, so that the curve representing the variation of the index of refraction with concentration is nearly a straight line:

C .	0·048	0·145	0·290	0·386	0·483	0·579	0·869	0·965
μ .	1·32711	1·32989	1·33436	1·33726	1·33978	1·34320	1·35018	1·35285

F. Flöttmann studied the subject; A. Huber, F. Allison and E. J. Murphy, the magneto-optical properties; P. Niggli, the reflexion maxima; T. Swensson, the photoelectric properties of the sulphate; and H. Nisi, and P. Krushamurti, the **Raman effect.**

S. B. Elings and P. Terpstra studied the **piezoelectricity** of crystals of the heptahydrate. E. Franke found the eq. **electrical conductivity,** λ, of soln. of an eq. of nickel sulphate in v litres of water, at 25°, to be:

v . . .	32	64	128	256	512	1024
λ . . .	66·7	77·4	88·2	98·9	109·3	117·4

and H. C. Jones added that the conductivity increases regularly from the most dil. soln. to the most conc. soln. employed. Observations were made by E. Bouty, E. Klein, N. Tarugi and G. Bombardini, and K. Murata. A. Deubner and A. Dobenzig studied the increase in the conductivity when sodium chloride is added to the solution. H. Rieckhoff and H. Zahn studied the high frequency conductivity. H. C. Jones and C. A. Jacobson found for the mol. conductivity, μ, of soln. with a mol of nickel sulphate in v litres of water at 0° and 25°; with the corresponding temp. coeff., a; and the **percentage ionization,** α:

v	. .	2	8	32	128	512	1024	2048
μ	0° .	28·77	40·38	54·78	73·95	93·12	100·4	108·3
	25° .	54·58	77·06	103·5	140·3	177·5	193·8	208·7
a	0°–10°	0·96	1·38	1·84	2·59	3·16	3·44	3·72
	10°–25°	1·08	1·50	2·01	2·69	3·52	3·93	4·21
	25°–35°	0 98	1·39	1·95	2·81	3·60	4·08	4·52
α	0° .	26·6	37·5	50·6	68·3	86·0	92·7	100·0
	25°. .	26·2	36·9	49·6	67·2	85·1	92·9	100·0

C. A. L. de Bruyn and C. L. Jungius, and G. Bruni and A. Manuelli made observations on the conductivity of alcoholic soln. L. Kahlenberg and co-workers calculated 0·048 per cent. for the **hydrolysis** of 0·5N-$NiSO_4$ at 55·5°; and H. G. Denham, for soln. with a mol of the salt in 4 to 64 litres of water at 32°, 0·044 per cent. $Ni^{\cdot\cdot}+2H_2O \rightleftharpoons Ni(OH)_2+2H^{\cdot}$, where the equilibrium constant $K=1{\cdot}1\times10^{-13}$. Hence cobalt sulphate is less hydrolyzed than nickel sulphate in aq. soln. R. Saxon studied the electrolysis of soln. of the sulphate associated with other metal sulphates. The **electrodeposition** of nickel from soln. of the sulphate was studied by R. Böttger, E. and A. C. Becquerel, R. Kayser, G. Gore, J. Powell, and M. Hess—*vide supra.* D. J. G. Ives studied the electrometric titration of the sulphate. J. B. O'Sullivan buffered a soln. of nickel sulphate with acetate, phosphate, and borate, and found that the value of P_H was lowered from 5. The **electrodeposition potential** (*q.v.*) was studied by F. Förster and K. Georgi; the potential-current curve, by J. Liger, and N. Nekrassoff and co-workers; and the electrodeposition of nickel from soln. of the sulphate has been previously discussed. J. B. O'Sullivan studied the electrometric titration of buffered soln. A. Coehn and M. Gläser measured the **anodic decomposition** curves for nickel sulphate in aq. soln., and in soln. slightly alkaline or acidic. I. Lifschitz and S. B. Hooghoudt studied the **Becquerel effect** in ultra-violet light. **Electrostenolysis** has been produced with soln. of cobalt sulphate but not with soln. of nickel sulphate. J. M. Merrick obtained what he called *nickel subsulphate* as a film on electrodeposited nickel. A. C. Becquerel observed that when a soln. of nickel sulphate, treated with a little alkali hydroxide to neutralize the excess of acid, is electrolyzed, a white precipitate with a yellow crust is formed. R. Saxon studied the electrodeposition of nickel from mixed soln. of nickel and cobalt sulphates. N. Isgarischeff and N. Kudrjawzeff studied

the effect of an alternating current on the electrolysis of soln. of nickel sulphate. E. Bouty discussed the **thermoelectric force** of aq. soln.

J. Grailich and V. von Lang, H. Nisi, H. Mosler, C. J. Gorter and co-workers, R. A. Fereday, E. C. Wiersma, B. Cabrera and co-workers, W. J. de Haas and E. C. Wiersma, H. Mosler, K. S. Krishnan and co-workers, R. H. Weber, A. Serres, P. Théodoridès, D. S. Kothari, and G. Foëx studied the **magnetic properties** of hydrated nickel sulphate. The paramagnetism parallel to the vertical axis was found by J. Grailich and V. von Lang to be strongest, and that parallel to the *b*-axis, weakest. W. Finke measured the magnetic susceptibility of the heptahydrate in the different axial directions, and for *a*, *b*, and *c*, respectively, obtained $29{\cdot}0\times10^{-6}$, $29{\cdot}23\times10^{-6}$, and $29{\cdot}95\times10^{-6}$ mass unit. G. Jäger and S. Meyer gave for the magnetic susceptibility of aq. soln. 25×10^{-6} mass unit at 18°; O. Liebknecht and A. P. Wills, 28×10^{-6} mass unit at 18°; J. Königsberger, 33×10^{-6} mass unit at 22°; G. Quincke, 34×10^{-6} mass unit at 19°; and G. Meslin, 19×10^{-6} mass unit. W. Finke gave for the crystals of the heptahydrate, 18×10^{-6} vol. unit. L. C. Jackson's results for the reciprocal of the mol. magnetic susceptibility of the heptahydrate, and of the anhydrous salt, are summarized in Fig. 351. W. J. de Haas and E. C. Wiersma, S. Datta, R. A. Fereday, J. Forrest, R. B. James, E. F. Herroun, A. Serres, B. Bavink, G. Foëx, E. C. Stoner, and W. Sucksmith studied the subject. T. Ishiwara measured the magnetic susceptibility, χ mass units, of anhydrous nickel sulphate at low temp., and K. Honda and T. Ishiwara at high temp., and found:

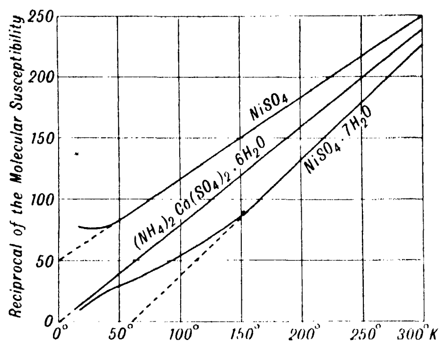


FIG. 351.—The Effect of Temperature on the Molecular Magnetic Susceptibility of Nickel Sulphate.

	−182·8°	−105·8°	−52·5°	6·1°	103·1°	264·3°	504·1°	762·7°
$\chi\times10^{6}$.	68·4	42·7	34·8	28·5	22·0	16·8	12·4	10·2

W. König moulded the salt in gelatin and measured the susceptibility when deformed. B. Cabrera and A. Duperier also studied the effect of temp. on the magnetic susceptibility. C. J. Gorter and co-workers could not verify the existence of the anomalies observed by L. C. Jackson and H. K. Onnes. D. Samuracas, and E. W. R. Steacie and C. F. B. Stevens found that the rate of crystallization of the sulphate from an aq. soln. is accelerated in a magnetic field.

The chemical properties of nickel sulphate.—A. Dobroserdoff found that the crystals of the sulphate are not decomposed by exposure to **light.** If the crystals occupy only a small portion of the containing vessel, they lose water with the formation of the hexahydrate, whether they are exposed to light or not. On the other hand, they are not changed, even by strong light, if the surrounding air is saturated with water vapour or if the crystals are in contact with filter paper moistened with turpentine, or if they completely fill the vessel containing them. G. P. Schweder, and E. Donath observed that when nickel sulphate is heated in **hydrogen,** some nickel sulphide is formed; J. H. Weibel studied the reaction, and S. Miyamoto noted that salt is reduced by hydrogen in the silent discharge. L. Meyer observed that the sulphate acts as a carrier of **oxygen** in catalyzed reactions. G. Gire found basic nitrates are precipitated from the solution by magnesium. A. Mailfert said that the anhydrous sulphate is slowly attacked by **ozone,** forming some nickelic oxide.

K. Jablczynsky and co-workers found that the rate of dissolution in **water** and non-aqueous solvents follows the same rules as those of less soluble salts; and

F. Foreman found that steam is decomposed by the heated sulphate. The solubility of the salt in water has been previously discussed; and, as indicated above, the salt in aq. soln. is very slightly hydrolyzed. J. Traube and W. von Behren found that submicrons of the salt are developed during dissolution. R. Tupputi thought that a basic sulphate is formed during the partial roasting of nickel sulphate; J. M. Merrick, by the electrolysis of a soln. of nickel sulphate; O. L. Erdmann, by igniting nickel amminosulphate; and J. J. Berzelius, by precipitation from soln. of the sulphate by the addition of an amount of alkali hydroxide insufficient for complete precipitation. A. Marshall added that unless a large excess of ammonium salt or free ammonia is present, dil. ammoniacal soln. of nickel sulphate are apt to deposit a basic sulphate; in one case, 60 per cent. of the nickel in soln. was precipitated as $NiSO_4.8NiO.16H_2O$. J. Habermann obtained **nickel oxysulphate,** $7NiO.SO_3.10H_2O$, in a similar manner; and P. de Clermont obtained $7NiO.SO_3.nH_2O$, by exposing moist nickel sulphide to the atmosphere. W. Feitknecht found that the lattice of $NiSO_4.3Ni(OH)_2$ corresponds with alternate layers of hydroxide and normal salt. D. Strömholm reported an amorphous product, $6NiO.SO_3$; and N. Athanasesco, pale, microscopic needles of $6NiO.5SO_3.4H_2O$, formed by boiling a soln. of the neutral sulphate with one-fifth part of nickelous or barium carbonate for 5 to 8 hrs., and then heating the filtrate in a sealed tube at 230° to 240°. S. U. Pickering reported the formation of $5NiO.3SO_3$, of $5NiO.2SO_3$, and of $5NiO.SO_3$, when alkali lye is added to a soln. of nickel sulphate. All this is unsatisfactory evidence of the formation of the existence of an oxysulphate as a chemical individual. According to H. Fuchs, when nickel hydroxide is shaken with soln. of 5 to 25 grms. of hydrated nickel sulphate in 100 grms. of soln., until equilibrium is attained, there is formed a basic salt which can be dried on a porous tile. Its composition corresponds with **nickel tetroxysulphate,** $NiSO_4.4NiO.14H_2O$, or $[(H_2O.H_2O)_2.Ni.(ONi.H_2O.H_2O)_4]SO_4(H_2O)_2$; the salt was also obtained by G. Gire. The vap. press. curve of this salt shows that 4 mols. of water are lost over conc. sulphuric acid to form the *decahydrate*, $[(H_2O.H_2O)_2Ni.(ONi.H_2O)_4]SO_4(H_2O)_2$; and at 100°, 5 mols of water are given off. The *enneahydrate* is accordingly taken to be the more stable form. By shaking the tetroxysulphate with soln. containing 2·5 to 25 grms. of hydrated nickel sulphate in 100 grms. of water until equilibrium attained there is formed nickel dioxysulphate, $NiSO_4.2NiO.10H_2O$. W. von Behren and J. Traube studied the submicrons of the sulphate in aq. soln.

E. J. Mills and co-workers discussed the simultaneous precipitation of nickel and manganese carbonates, and of nickel and cadmium carbonates, by adding sodium carbonate to soln. of the sulphate. According to G. Watson, when **hydrogen dioxide** is added to an ammoniacal, not an acidified, soln. of nickel sulphate, oxygen is evolved—but no evidence of the formation of a peroxide was observed. A. W. Hothersall and R. A. F. Hammond, and R. Kuhn and A. Wassermann studied the reaction. C. Hensgen observed that the anhydrous sulphate is not attacked by **hydrogen chloride** at ordinary temp., or at 100°. R. J. Kane found that a mol. of nickel sulphate absorbs a mol. of hydrogen chloride with the evolution of heat. The gas is given off on exposure to air. The aq. soln. yields crystals of the heptahydrated sulphate. F. Ephraim said that the sulphate does not unite additively with hydrogen chloride. D. Costeanu and A. St. Cocosinschi studied the action of hydrochloric acid. S. E. Moody found that the hydrolysis of soln. of nickel sulphate by mixtures of **potassium iodide and iodate** is in accord with the equation: $3NiSO_4+5KI+KIO_3+3H_2O=3Ni(OH)_2+3K_2SO_4+3I_2$, and that the reaction is complete if the liberated iodine is removed by a current of hydrogen.

P. de Clermont noted that a soln. of nickel sulphate has a perceptible solvent action on flowers of **sulphur.** H. Baubigny observed that when the sulphate is heated with an aq. soln. of **hydrogen sulphide** in a sealed tube, crystals of nickel sulphide are formed. Hydrogen sulphide precipitates from the neutral, dil. or

conc. soln. of nickel sulphate, nine-tenths of the nickel as sulphide in 48 hrs., and in 32 days, all the nickel is precipitated. It is all the same whether the soln. be sat. at 0° or at 30°; the precipitation proceeds more slowly with the more dil. soln. of hydrogen sulphide. The sulphuric acid which is liberated in the reaction: $NiSO_4+H_2S\,aq.\rightleftharpoons NiS+H_2SO_4aq.$, retards the precipitation of the sulphide. E. Pietsch and co-workers studied the action of an alcoholic or alcohol-ether soln. of hydrogen sulphide. J. Myers observed that when nickel sulphate is heated with **potassium sulphide,** nickel and alkali polysulphide are formed. J. Kendall and A. W. Davidson observed no evidence of the formation of *nickel hydrosulphate;* and they found that the neutral salt is slightly soluble in conc. **sulphuric acid**—the clear yellow soln. contains 0·25 mol. per cent. of $NiSO_4$, and furnishes, on crystallizing, solid Ni_2SO_4. A mixture containing 0·29 mol. per cent. of nickel sulphate did not all dissolve, even on boiling. L. McCulloch also noted the sparing solubility of nickel sulphate in sulphuric acid. C. Montemartini and L. Losana studied the solubility of the salt in sulphuric acid, and in soln. of potassium sulphate. H. Brintzinger and H. Osswald studied the complex sulphates $[Ni_2(SO_4)]^{4-}$. Nickel sulphate undergoes a number of metathetical reactions—*e.g.*, C. F. Rammelsberg observed that when **strontium thiosulphate** is added to the soln. of nickel sulphate, nickel thiosulphite appears when the soln. is evaporated; and J. T. Norton, that when the sulphate is heated with **sodium thiosulphate** in a sealed tube at 140° to 200°, nickel sulphide and sulphur are formed.

According to E. C. Franklin and C. A. Kraus, anhydrous nickel sulphate is insoluble in liquid **ammonia.** W. R. Hodgkinson and C. C. French studied the reduction of the sulphate when it is heated in ammonia gas. H. Rose said that the anhydrous sulphate absorbs ammonia gas with intumescence, and the development of much heat, forming **nickel hexamminosulphate,** $NiSO_4.6NH_3$, or $[Ni(NH_3)_6]SO_4$. M. A. Rakuzin and co-workers, E. Kocsis, and O. R. Foz and L. le Boucher studied the amminosulphates. According to H. Rose, the pale violet hexammine gives off ammonia, water, and ammonia sulphite when it is moderately heated, and the yellow residue dissolves in water except for some reduced nickel. The ammine may be blackened by a sudden rise of temp. owing to the presence of reduced nickel. F. Müller gave 146° for the temp. of dissociation —*vide infra.* F. Ephraim observed that the decomposition press., p mm., of the freshly-prepared and aged (6 months) hexammines differ:

	100·5°	111°	122·5°	131·5°	134°
Fresh p . .	170	257	441	673	752
	91°	109·8°	123·5°	135°	144·5°
Aged p . .	62	190·8	338	525	810

E. Lohmann, and Y. Shibata studied the absorption spectrum; W. Vethake, the mol. refraction; and R. A. Fereday, and D. M. Bose, the magnetic properties. According to H. Rose, the hexammine dissolves in water, forming a blue soln., and a precipitate of green nickel hydroxide. P. Mosimann found the solubility in water to be 14·22 grms. or 0·055 mol. of nickel sulphate per litre. H. M. Dawson and J. McCrae studied the formation of the ammines in aq. soln.; and S. G. Mokruschin and E. I. Kriloff, the surface energy.

According to F. Ephraim, the thermal decomposition of the hexammine furnishes **nickel tetramminosulphate,** $NiSO_4.4NH_3$, and there is no perceptible difference in the dissociation press., p mm., of the products derived from the freshly-prepared and the aged hexammine:

	136°	151·5°	163·5°	170·5°	175°
p	88	143	350	550	717

The tetrammine is best obtained by heating the hexammine to 135° to 137°. D. M. Bose studied the magnetic properties. The product of the decomposition of the tetrammine is pale yellow **nickel diamminosulphate,** $NiSO_4.2NH_3$. The

diammine is best obtained by heating the hexammine or tetrammine to 177·5°. W. V. Bhagwat studied the absorption spectrum. The diammine at 335° yields **nickel monamminosulphate,** $NiSO_4.NH_3$; and this, in turn, above 380°, yields **nickel hemiamminosulphate,** $2NiSO_4.NH_3$. K. J. S. King and co-workers prepared **nickel aquopentamminosulphate,** $[Ni(NH_3)_5(H_2O)]SO_4$. O. L. Erdmann found that conc. aq. ammonia colours blue an aq. soln. of nickel sulphate; and crystals of **nickel diaquotetramminosulphate,** $NiSO_4.4HN_3.2H_2O$, or $[Ni(NH_3)_4(H_2O)_2]SO_4$, are formed when the soln. is cooled, when it is concentrated by evaporation in vacuo over sulphuric acid, or by treatment with alcohol. The salt can be recrystallized by dissolving it in the smallest required proportion of warm water, and cooling. The dark blue prismatic crystals crumble to a light blue powder on exposure to air, or in vacuo. When heated in a glass tube, ammonia, ammonium sulphate, and a greenish-grey powder, presumably basic nickel sulphate, are formed. Y. Shibata studied the absorption spectrum. According to O. L. Erdmann, the conc. aq. soln. gives off ammonia when it is boiled, and deposits green flakes of nickel hydroxide contaminated with sulphate. The salt is insoluble in alcohol even when diluted with water. G. André reported the aquoammine $2NiSO_4.5NH_3.7H_2O$—that is, $[Ni_2(NH_3)_5(H_2O)_7](SO_4)_2$—to be formed in pale violet, deliquescent needles, by passing ammonia through a well-cooled soln. of nickel sulphate. E. Kocsis studied these salts.

T. Curtius and F. Schrader added **hydrazine hydrate** to a soln. of nickel sulphate, and obtained **nickel trihydrazinosulphate,** $NiSO_4.3N_2H_4$, as a pale reddish-violet precipitate which does not dissolve in an excess of the precipitant. A similar precipitate is obtained by heating an aq. soln. of hydrazine nickel sulphate. H. Franzen and O. von Mayer obtained the trihydrazine sulphate by adding hydrazine hydrate to an ammoniacal soln. of nickel sulphate. C. Paal and L. Friederici also studied the action of hydrazine on nickel sulphate; and S. Datta, the magnetic susceptibility of the salts. F. Ephraim and P. Mosimann, and R. Uhlenhuth added **hydroxylamine** to a cold, sat. soln. of nickel sulphate, and noted that the blue soln. first formed soon becomes red, and after the red soln. has stood for some time, it deposits red, triclinic crystals of **nickel hexahydroxylaminosulphate,** $[Ni(NH_2OH)_6]SO_4$. The addition of a few drops of alcohol favours the separation of the crystals, but if too much alcohol is employed, the crystals are impure, and if the soln. are not sufficiently concentrated, the precipitate is white. The salt decomposes when washed with water, or alcohol, and a white powder is formed. When the salt is heated, it swells up, becomes blue, and then almost white. W. Manchot and co-workers observed that soln. with 14·449 and 28·998 grms. of $NiSO_4$ per 100 c.c. dissolve, respectively, 24·9 and 14·2 c.c. of **nitrous oxide** per 100 c.c. C. Paal and L. Friederici found that **sodium hypophosphite** acts on an aq. soln. of nickel sulphate, producing a nickel phosphide.

According to J. L. Gay Lussac, when a mixture of anhydrous nickel sulphate and **carbon** is heated, equal vols. of carbon and sulphur dioxides are evolved, and there remains nickel mixed with a little sulphide. E. Donath, and G. P. Schweder also noted that the salt is reduced when it is heated in a current of **carbon monoxide.** J. H. Weibel studied the reaction. W. Manchot and co-workers observed that soln. with 11·42 and 22·84 grms. of $NiSO_4$ per 100 c.c. dissolve, respectively, 60·1 and 38·5 c.c. of **acetylene** per 100 c.c. K. Masaki studied the action of **potassium cyanide**; S. Papiermeister observed that a complex ammine is formed when **mercuric cyanide** is added to an alcoholic soln. of nickel sulphate. C. A. L. de Bruyn observed that after anhydrous nickel sulphate had been in contact with absolute **methyl alcohol** for 8 to 9 months, only 1·34 per cent. was dissolved. With hydrated alcohol, the complex **nickelous sulphate trialcoholate,** $NiSO_4.3CH_3OH.3H_2O$, is formed. The solubility of this complex, represented by S per cent. $NiSO_4$ in the sat. soln., at 14°, is:

CH_3OH .	100	97·5	95	90	88	85 per cent.
S . . .	3·72	0·77	0·455	0·70	1·25	1·93 ,,

100 parts of absolute methyl alcohol dissolve 46 parts of the heptahydrate at 17°, and 24·7 parts at 4°; 100 parts of 93·5 per cent. methyl alcohol dissolve 10·1 parts of the heptahydrate at 4°, and 100 parts of 93·5 per cent. methyl alcohol dissolve 2 parts of the heptahydrate at 4°. The solubility, *S* per cent. $NiSO_4$, of the heptahydrate in aq. soln. of methyl alcohol at 14°, is:

CH_3OH	100	95	85	82	80	60	40	20	0 per cent.
S . .	16·8	11·6	1·52	0·83	0·653	0·805	2·78	13·7	26·4 ,,

The minimum occurs with 80 per cent. alcohol. With the α- and β-hexahydrates as solid phases, the solubility, *S* per cent. of $NiSO_4$, in methyl alcohol at 14°, is:

CH_3OH . .	100	95	85	80	60	40	20	0 per cent.
S {α . .	12·4	6·5	0·315	0·25	0·46	2·43	14·7	26·0
S {β . .	15·7	10·0	0·61	0·415	0·75	3·11	14·1	27·2

The solubilities of the tetrahydrate, at 10°, in 100, 80, 50, 20, and 0 per cent. of aq. methyl alcohol are, respectively, 7·38, 0·66, 1·43, 14·8, and 25·1 per cent. Nickel sulphate is more soluble in **ethyl alcohol** than it is in methyl alcohol; 100 parts of absolute ethyl alcohol dissolve 1·3 grms. of the heptahydrate at 4°, and 2·2 grms. at 17°. G. C. Gibson and co-workers gave for the solubility of $NiSO_4$ in alcohol, *S* grm. of salt per gram of alcohol:

	15°	25°	35°	45°	55°
S {Methyl alcohol .	0·00061	0·00081	0·00110	0·00157	0·00222
S {Ethyl alcohol .	0·00017	—	0·00020	0·00022	0·00025

K. P. MacElroy and W. H. Krug found that nickel sulphate is very slightly soluble in **acetone,** but A. Naumann, and W. Eidmann said that it is insoluble. F. W. O. de Coninck found that 100 grms. of a sat. soln. in **glycol** contain 9·7 grms. $NiSO_4$, at ordinary temp. A. Recoura observed that with **acetic anhydride,** nickel sulphate forms $NiSO_4.(C_2H_3O_2)_2O.H_2O$. J. Persoz said that glacial **acetic acid** precipitates nickel sulphate from its aq. soln. A. Naumann found nickel sulphate to be insoluble in **methyl acetate,** and also in **ethyl acetate,** and W. Wislicenus and W. Stoeber added that an ammoniacal soln. of nickel sulphate forms a basic salt when treated with ethyl acetate. S. Glasstone and co-workers studied its effect on the solubility of ethyl sulphate in water. M. Duyk observed that nickel sulphate is reduced to a brown oxide by **sugars.** S. Hakomori studied the action of **oxalic acid,** and of **citric acid** on nickel sulphate; and J. P. Mathieu, the action of **tartaric acid.**

F. K. V. Koch studied the distribution of **pyridine** between benzene and an aq. soln. of nickel sulphate. F. Reitzenstein, G. Spacu and R. Ripan, L. Pincussohn, H. von Euler, and W. Lang studied **nickel trispyridinosulphate,** $[Ni(C_5H_5N)_3]SO_4.2H_2O$; and J. Dalietos, **nickel pyridinosulphate,** $[Ni(C_5H_5N)]SO_4$. G. Spacu and R. Ripan prepared **potassium nickel aquoquinquiespyridinosulphate,** $[Ni\,py_5(H_2O)](KSO_4)_2$; and U. Pomilio prepared **nickel bisquinolinosulphate,** $Ni(C_9H_7N)_2SO_4$. A. Werner and W. Megerle, E. Schürmann, and J. Dalietos observed that **ethylenediamine** forms with nickel sulphate, **nickel tetraquoethylenediaminosulphate,** $[Ni\,en(H_2O)_4]SO_4$, and E. Rosenbohm measured the magnetic susceptibility of the salt. A. Werner and W. Spruck, and A. Grünberg prepared **nickel trisethylenediaminosulphate,** $[Ni\,en_3]SO_4$; J. Angerstein studied the absorption spectrum; and E. Rosenbohm, the magnetic susceptibility; and A. Grünberg, some reactions of the salt. J. Dalietos and E. Lohmann, reported **nickel diaquobisethylenediaminosulphate,** $[Ni\,en_2(H_2O)_2]SO_4$. P. Pfeiffer and F. Tappermann studied the complex with **phenanthroline.** L. Tschugaeff found that **trimethylenediamine** forms **nickel bistrimethylenediaminosulphate,** $[Ni(NH_2.CH_2.CH_2.CH_2.NH_2)_2]SO_4$; and R. Cernatescu and M. Papafil, that phenylenediamine forms **nickel bisphenylenediaminosulphate,** $[Ni\{o\text{-}C_6H_4(NH)_2\}]SO_4$; W. Hieber and E. Levy, a complex with **monoethylolamine;** A. Tettamanzi and B. Carli, one

with **triethanolamine**; K. A. Jensen, and K. A. Jensen and E. Rancke-Madsen, a complex with **thiosemicarbazide**; A. Werner and J. Pastor found that propylenediamine forms **nickel trispropylenediaminosulphate,** $[Ni(C_3H_6N_2H_4)_3]SO_4$; F. G. Mann and W. J. Pope, **nickel bistriaminopropanosulphate,** $[Ni(NH_2.CH_2.CH(NH_2).CH_2.NH_2)_2]SO_4.5H_2O$; J. Frejka and L. Zahlova, **nickel trisbutylenediaminosulphate,** $[Ni\ bn_3]SO_4.4H_2O$; W. Hieber and co-workers, **o-phenylenediamine**; F. M. Jäger and J. A. van Dijk, **dipyridyl**; G. Spacu and R. Ripan, potassium **nickel diaquobisbenzylaminosulphate,** $[Ni(NH_2.CH_2.C_6H_5)_2(H_2O)_2](KSO_4)_2$; and M. R. Menz, a complex with **hexamethylenetetramine.** E. Thilo and H. Heilborn obtained with **diacetyldioxime,** the unstable complex, **nickel bisdiacetyldioximosulphate,** $[Ni(CH_3CNOH)_2]SO_4$; G. Ponzio, **nickel bismethylhydroxyglyoximosulphate,** $[Ni(C_3H_6O_3N_2)_2]SO_4$; D. Tombeck, a complex with **aniline,** namely, **nickel hexanilinosulphate,** $[Ni(C_6H_5.NH_2)_6]SO_4$; and H. Schjerning, and J. Moitessier, a complex with **phenylhydrazine,** namely, **nickel phenylhydrazinosulphate,** $Ni(C_6H_5.N_2H_3)SO_4.H_2O$, and a complex with both aniline and phenylhydrazine. P. C. and N. Ray prepared a complex with **ethylphosphonium sulphate.** L. Meyer observed that no complex is formed with **thiocarbamide** either in alcoholic or aq. soln.; and K. A. Jensen, compounds with **thiosemicarbazide.** M. R. Menz prepared a complex with **camphidine**; and G. Canneri, one with **guanidine.** M. Berthon studied the adsorption of the salt from aq. soln. by **silica gel.**

According to G. Gire, and E. S. Hedges and J. E. Myers, a magnesium-nickel couple is formed when **magnesium** is dipped in a soln. of nickel sulphate. R. Kremann and co-workers found that **zinc** and **cadmium** will precipitate nickel from aq. soln. of the sulphate at room temp., and the precipitate contains both nickel, and nickel hydroxide. The proportion of hydroxide decreases with a rise of temp., and increases with the ratio of the zinc or cadmium to the precipitated nickel. M. Centnerszwer and W. Heller, and J. A. N. Friend and J. S. Tidmus studied the dissolution of zinc in soln. of nickel sulphate; and M. J. Salauze, the reduction of the soln. by **aluminium**; and T. Heymann and K. Jellinek, the reaction with **cobalt**: $Co+Ni^{\cdot\cdot} \rightleftharpoons Ni+Co^{\cdot\cdot}$. E. J. Mills and J. J. Smith studied the mutual

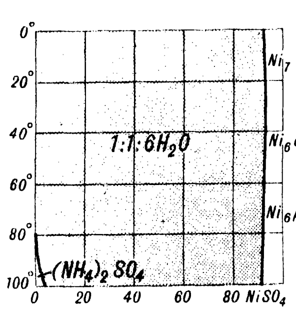


FIG. 352.—The Ternary System: $(NH_4)_2SO_4$–$NiSO_4$–H_2O.

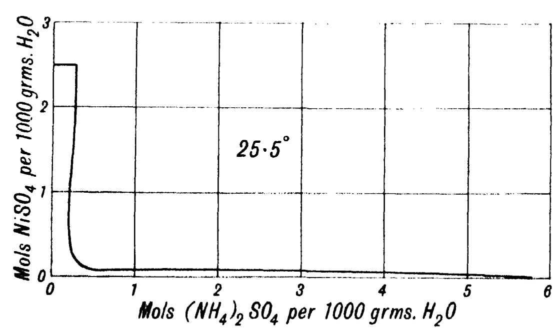


FIG. 353.—The Ternary System: $(NH_4)_2SO_4$–$NiSO_4$–H_2O at 25·51°.

precipitation of nickel and cobalt hydroxides by the addition of **sodium hydroxide** to a mixed soln. of nickel and cobalt sulphates; E. J. Mills and B. Hunt, nickel and cadmium sulphates; E. J. Mills and J. H. Becket, nickel and manganese sulphates; W. Schopper, the precipitation of nickel hydroxide from a soln. of the sulphate by **quicklime** or **limestone**; A. W. Wellings, the titration of the soln. with standard **barium hydroxide**; and L. S. Levy, the adsorption of the salt by **manganese dioxide.** R. Schenck and E. Raub studied the reaction of the salt with **nickel sulphide** (*q.v.*); O. Ruff and B. Hirsch, the action of **ferrous sulphide,** of **manganese sulphide,** and of **zinc sulphide.**

The double salts of nickel sulphate.—H. F. Link,[2] and E. Mitscherlich

obtained **ammonium nickel disulphate,** $(NH_4)_2Ni(SO_4)_2.6H_2O$, from mixed soln. of the component salts, and the process was described in detail by O. Aschan, R. M. Caven, S. P. L. Sörensen, C. Künzel, L. Thompson. P. Dirvell, and G. Delvaux. A. Benrath's study of the system $(NH_4)_2SO_4$–$NiSO_4$–H_2O is summarized in Fig. 352. The region of formation of the 1 : 1 : 6 double salt is stippled, and Ni6α, Ni6β, and Ni7, respectively, refer to the α- and β-hexahydrates, and the heptahydrate of nickel sulphate. R. M. Caven and W. K. Gardner's results are summarized in Fig. 353.

The bluish-green crystals of the double salt were found by A. Murmann and L. Rotter to be monoclinic prisms with the axial ratios $a : b : c = 0{\cdot}7370 : 1 : 0{\cdot}5032$, and $\beta = 107°\ 4'$. Observations were also made by J. C. G. de Marignac, and H. de Sénarmont. A. E. H. Tutton gave $0{\cdot}7373 : 1 : 0{\cdot}5000$, and $\beta = 106°\ 57'$. The habit is prismatic, parallel with the (011)-face. The (001)- and (110)-faces are sometimes striated. The cleavages parallel to the (201)- and the (010)-faces are good. The optic axial angles are :

	Li-	*C*-	Na-	Tl-	Cd-	*F*-lines
$2H_a$ . . .	76° 30′	76° 28′	76° 8′	75° 50′	75° 40′	75° 29′
$2H_o$ . . .	82° 24′	82° 20′	81° 50′	81° 24′	81° 5′	80° 50′
$2V_a$ . . .	86° 27′	86° 28′	86° 33′	86° 37′	86° 40′	86° 43′

E. Mitscherlich observed that the crystals are isomorphous with those of ammonium magnesium sulphate, and with the corresponding ammonium cobalt sulphate. According to A. E. H. Tutton, the molecular distance ratios, *i.e.* the topical axial ratios, are $\chi : \psi : \omega = 6{\cdot}1426 : 8{\cdot}3312 : 4{\cdot}1656$. The sp. gr. is 1·923 at 20°/4°. F. L. Perrot gave 1·922 for the sp. gr. ; L. Thompson, 1·801 ; H. Kopp, 1·915 ; and H. Schröder, 1·921. The subject was discussed by J. A. Groshans. A. E. H. Tutton gave 203·91 for the mol. vol., and F. L. Perrot, 205. G. Quincke gave 1·041 at 19°/4°, for the sp. gr. of a 4·89 per cent. aq. soln. According to W. A. Tilden, the salt, when heated, gives off water without melting. R. M. Caven and J. Ferguson observed the vap. press., p mm., of the hexahydrate, to be :

	33·5°	43·2°	53·7°	68·8°	72·8°
p . . .	1·6	4·1	9·2	24·3	31·9

or $\log p = 2{\cdot}370 + 2437T^{-1} - 1{,}249{,}600T^{-2}$, the dihydrate is formed when the salt is heated. The heat of hydration of the dihydrate is 15·4 Cals. per mol. of water vapour. The subject was discussed by F. Ephraim and P. Wagner. E. Rouyer examined the elevation of the b.p. of mixed soln. of the component salts. A. E. H. Tutton gave for the refractive indices :

α . . .	1·4906	1·4921	1·4949	1·4976	1·4993	1·5007	1·5060
β . . .	1·4975	1·4980	1·5007	1·5037	1·5052	1·5069	1·5123
γ . . .	1·5046	1·5051	1·5081	1·5110	1·5125	1·5142	1·5196

The mean value for Na-light is 1·5012. H. de Sénarmont gave 1·499. According to A. E. H. Tutton, the general formula for the refractive index, β, corrected to a vacuum, is $\beta = 1{\cdot}4873 + 472{,}952\lambda^{-2} + 212{,}960{,}000{,}000\lambda^{-4} + \ldots$ The α-indices are reproduced very closely if the constant 1·4873 is reduced to 1·4813 ; and the γ-indices, if this constant be 1·4946. At 70°, the refractive indices are decreased by 0·0018° for α, to 0·0022° for γ for a 55° rise of temp. The double refraction for Na-light is $\gamma - \alpha = 0{\cdot}0132$. The sp. refractions with the μ^2-formula for the $C(H_\alpha)$- and H_γ (near G)-rays are, respectively, $\alpha = 0{\cdot}1509$, and 0·1545.

According to W. Pfanhauser, the electrical conductivity of the more conc. soln. of the salt in aq. soln. is less than the sum of the conductivities of the constituent salts, and this indicates that complex ions are formed. This is confirmed by measurements of the transport numbers, which show that in the sat. soln., at 18°, $NH_4^{\cdot}$-ions and $Ni(SO_4)_2''$-ions are present ; but with more dil. soln. NH_4'-, $Ni^{\cdot\cdot}$-, and SO-″-ions are formed. Taking the calomel electrode as −0·56 volt, the electrode potentials of the following metals in N-$NiSO_4$, and N-$(NH_4)_2Ni(SO_4)_2$, were, respectively : nickel, −0·041 and −0·060 volt ; lead, −0·005 and −0·007

volt; zinc, 0·482 and 0·493 volt; copper, −0·569 and −0·591 volt; and nickelic hydroxide, −1·135 and −1·152 volts. Polarization occurs in the electrolysis of soln. of nickel sulphate or of the double salt with nickel electrodes. The lower value, 1·06 volts, corresponds with the decomposition of water, and the evolution of oxygen at the anode; and the higher value, about 2·3 volts in neutral, and 1·9 volts in acidic soln., is due to the formation of nickelic sulphate at the anode, and its immediate hydrolysis to nickelic hydroxide. The deposition of nickel in the electrolysis of a soln. of the salt was studied by R. Böttger, E. Gaiffe, M. Hesz, M. Martin and M. Delamotte, H. Meidinger, J. M. Merrick, S. P. Sharples, and F. Stolba—*vide supra*. H. Moehle gave $0·983 \times 10^{-6}$ mass unit for the magnetic susceptibility of the salt; and W. Finke gave for the three axial directions, $a=19·57\times10^{-6}$, $b=15·75\times10^{-6}$, and $c=17·98\times10^{-6}$ mass unit for the hexahydrate. B. W. Bartlett, A. Serres, I. I. Rabi, N. S. Krishnan and co-workers, and R. A. Fereday studied the subject. L. C. Jackson's results for the effect of temp. are indicated in Fig. 351.

H. F. Link found that the salt dissolves in about four times its weight of cold water; and measurements of the solubility were made by G. Quincke. C. von Hauer said that a soln. sat. at 20° contains 9·4 per cent. of the anhydrous salt; 13·2 per cent. at 40°; 18·6 per cent. at 60°; and 23·1 per cent. at 80°. J. Locke found that a litre of water, at 25°, dissolves 75·7 grms. of anhydrous salt. E. Tobler found the solubility, S grms. of anhydrous salt per 100 grms. of water, to be:

	3·5°	10°	16°	20°	30°	50°	68°	85°
S . .	1·8	3·2	5·8	5·9	8·3	14·4	18·8	28·6

R. Lattey gave for the percentage solubility, S,

	0°	10°	20°	30°	50°	70°	90°	100°
S . .	4·05	5·11	6·46	8·09	12·22	17·50	23·93	27·57

The data are summarized in Fig. 354, and the solubility in mols. per litre can be represented by $(141+3·2\theta+0·05\theta^2)\times10^{-4}$. A. W. Wellings studied the titration of the salt with a standard soln. of barium hydroxide. L. Thompson found that the salt is nearly insoluble in a soln. of ammonium sulphate. E. Alberts studied the action of carbon dioxide; and B. V. Nerasoff, the adsorption of the salt from soln. by charcoal. According to G. André, **ammonium nickel hexamminosulphate**, $(NH_4)_2Ni(SO_4)_2.6NH_3.1\frac{1}{2}H_2O$, is formed when ammonia is passed into a soln. of ammonium sulphate carrying nickel oxide in suspension in the proportions of a mol. of the oxide to 2 mols. of the ammonium sulphate, and the resulting liquid heated, and then allowed to cool. The same salt is produced when ammonia is passed into a soln. of the two sulphates in eq. proportions. The blue, rhombic prisms effloresce very rapidly on exposure to air, and ammonia is given off. The salt is decomposed by an excess of water with the separation of nickel hydroxide. Y. Shibata studied the absorption spectrum of the salt.

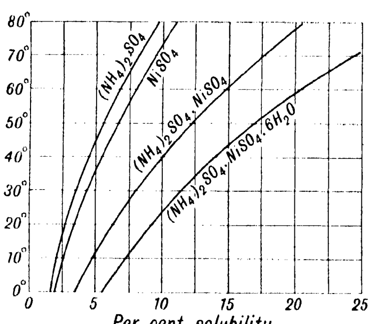


FIG. 354.—The Solubility of Ammonium Nickel Sulphate.

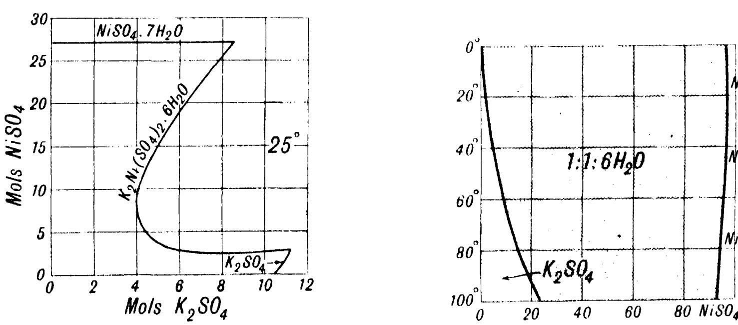
C. Lepierre and M. Lachaud obtained **ammonium nickelous pentasulphate**, $2(NH_4)_2SO_4.3NiSO_4$, by fusing anhydrous nickel sulphate or the oxide, hydroxide, or carbonate with five to six times its weight of ammonium sulphate. The deep yellow, tetrahedral, cubic crystals can be rapidly washed by cold water, and alcohol. The crystals soon become hydrated in contact with water, and much heat is developed. When heated with ammonium sulphate yellow octahedra of anhydrous nickelous sulphate are formed. H. Grossmann and B. Schück prepared

green triclinic crystals of **ethylenediamine nickel disulphate,** $C_2H_4(NH_2)_2Ni(SO_4)_2.6H_2O$; and T. Curtius and F. Schrader obtained **hydrazine nickel disulphate,** $(N_2H_5)_2Ni(SO_4)_2$, from mixed soln. of the component salts. The pale apple-green precipitate contains microscopic prisms. The salt is stable at 100°, but when heated to a higher temp. in a dry tube, it decomposes with the evolution of nitrogen, and sulphur dioxide, and leaves behind a mixture of nickel sulphate and oxide. Water at 18° dissolves 0·36 per cent. of the salt. The salt is insoluble in hydrochloric acid; it is decomposed by nitric acid with the evolution of gas; and it forms a blue soln. with aq. ammonia. When the ammoniacal soln. is heated, it deposits nickel trihydrazine sulphate.

J. L. Proust, L. Gmelin, E. Mitscherlich, and R. Tupputi prepared **potassium nickel disulphate,** $K_2Ni(SO_4)_2.6H_2O$, from mixed soln. of the component salts, or from a soln. of nickel oxide or carbonate in an aq. soln. of potassium hydrosulphate. F. R. Mallet reported yellowish-brown, tetrahedral crystals of the anhydrous salt to be formed by fusing a mixture of the component salts in theoretical proportions. The salt changes to the hexahydrate on exposure to air. R. M. Caven, C. Montemartini and L. Losana, and O. Aschan studied the formation of the salt. R. M. Caven and W. Johnston found that with the system K_2SO_4–$NiSO_4$–H_2O, at 25°, the solubilities, expressed in grams per 100 grms. of soln., or in mols per litre in Fig. 355, are:

K_2SO_4 .	10·59	11·16	4·93	5·62	8·26	6·30	3·82	0
$NiSO_4$.	0	0·33	1·35	19·33	27·90	27·92	27·87	27·94
Solid phase	K_2SO_4		$K_2SO_4.NiSO_4.6H_2O$			$NiSO_4.7H_2O$		

The results of A. Benrath's study of the same system are summarized in Fig. 356. The region of formation of the 1 : 1 : 6 salt is stippled; Ni6α, Ni6β, and Ni7 refer, respectively, to the α- and β-hexahydrates, and the heptahydrate of nickel sulphate.



FIGS. 355 and 356.—The Ternary System: K_2SO_4–$NiSO_4$–H_2O.

C. Montemartini and L. Losana studied the quaternary system: $NiSIO_4$–K_2SO_4–H_2SO_4–H_2O, between 0° and 25°, and observed the solid phases $NiSO_4$, $NiSO_4.2H_2O$, $KHSO_4.H_2O$, $KHSO_4.H_2SO_4$, $K_2SO_4.KHSO_4.H_2O$, and $K_2SO_4.NiSO_4.6H_2O$. A. Murmann and L. Rotter found that the bright green, or bluish-green transparent, tabular, or prismatic crystals are monoclinic, with the axial ratios $a:b:c$ 0·7374 : 1 : 0·4965, and β=105° 0′; and A. E. H. Tutton, 0·7379 : 1 : 0·5020, and β=105° 0′. Observations were also made by C. F. Rammelsberg, H. J. Brooke, and H. de Sénarmont. The optic axial angles were found by A. E. H. Tutton to be:

	Li-	C-	Na-	Tl-	F-
$2E$.	130° 18′	130° 23′	130° 57′	131° 34′	132° 22′
$2H_a$.	66° 53′	66° 47′	66° 26′	66° 6′	65° 37′
$2H_o$.	91° 6′	90° 56′	90° 33′	90° 7′	89° 9′
$2V_a$.	75° 21′	75° 19′	75° 16′	75° 13′	75° 9′

A rise of 50° increases the optic axial angle for Na-light by about 2·5°. The topic

axial ratios are $\chi:\psi:\omega=6\cdot0170:8\cdot1542:4\cdot0934$. H. Kopp gave 2·124 for the sp. gr.; H. Schröder, 2·212 to 2·231; and A. E. H. Tutton, 2·237 at 20°/4°, and the mol. vol. 193·99. The mol. vol. was discussed by F. Ephraim and P. Wagner. L. Playfair and J. P. Joule gave for the sp. gr. of the dihydrated salt, 2·897; and H. Schröder, 3·086. The crystals are stable in air, and, according to C. von Hauer, they lose only 0·12 per cent. of water at 100°. F. Rüdorff studied the rate of diffusion of 10 grms. of the salt in 100 grms. of water, and, after 12 hrs., found for 100 parts of nickel, 299 parts in the diffusate, and 133 parts of potassium in the salt. L. Gmelin, and J. I. Pierre observed that the salt fuses to a brown liquid at a low red-heat, and, on cooling, a yellow, crystalline mass is formed, which, according to H. Schröder, has a sp. gr. of 3·086, and when in contact with cold water, it gradually dissolves. The brown, anhydrous salt gradually gives the green hexahydrate when it is exposed to a moist atmosphere. At a bright red-heat, the salt decomposes into a mixture of nickel and potassium sulphate. R. M. Caven and J. Ferguson found the vap. press., p mm., of the hexahydrate to be:

	33·8°	45·1°	55·8°	64·8°	76·2°
p . . .	6·2	14·6	31·2	54·6	98·1

or $\log p=0\cdot981+3329T^{-1}-1{,}039{,}000T^{-2}$, as it passes into the dihydrate. The heat of hydration of the dihydrate is 14·1 Cals. per mol. of water vapour. A. E. H. Tutton observed that the refractive indices for light of different wavelengths, are:

	Li-	*C*-	Na-	Tl-	*F*-	*G*-rays
α . . .	1·4809	1·4813	1·4836	1·4860	1·4889	1·4933
β . . .	1·4889	1·4893	1·4916	1·4941	1·4972	1·5051
γ . . .	1·5022	1·5026	1·5051	1·5077	1·5109	1·5153

and the mean value for Na-light is 1·4934. The double refraction $\gamma-\alpha=0\cdot0215$. The indices of refraction are lowered by about 0·0012 for 50° rise of temp. H. de Sénarmont gave 1·490 for the mean index of refraction. A. E. H. Tutton found that the sp. refraction, with the μ^2-formula for the $C(H_\alpha)$- and the H_γ (near G)-rays are, respectively, $\alpha=0\cdot1273$, and 0·1300; $\beta=0\cdot1290$, and 0·1318; and $\gamma=0\cdot1321$, and 0·1349; the mol. refractions with the μ^2-formula, $\alpha=55\cdot23$, and 56·41; $\beta=56\cdot00$, and 57·20; and $\gamma=57\cdot31$, and 58·53; the mol. refractions with the μ-formula, $\alpha=93\cdot37$, $\beta=94\cdot92$, and $\gamma=97\cdot50$—mean$=95\cdot26$; the sp. dispersions for the G- and C-rays, $\alpha=0\cdot0027$, $\beta=0\cdot0028$, and $\gamma=0\cdot0028$; and the mol. dispersion, $\alpha=1\cdot18$, $\beta=1\cdot20$, and $\gamma=1\cdot22$. J. M. Merrick studied the electrolysis of a soln. of the salt. H. Moehle gave $0\cdot685\times10^{-1}$ mass unit for the magnetic susceptibility of the salt. N. S. Krishnan and co-workers, and R. A. Fereday studied the subject; and A. A. Lutheroth measured the effect of temp. on the magnetization. R. Tupputi found that the salt dissolves in eight to nine times its weight of cold water; C. von Hauer found the percentage solubility of the anhydrous salt to be 8·7 at 20°; 12·3 at 40°; 17·6 at 60°; and 22·0 at 80°. J. Locke found that, at 25°, a litre of water dissolves 68·8 grms. of the anhydrous salt. E. Tobler gave for the solubility, S grms. of anhydrous salt per 100 grms. of water:

	0°	10°	20°	30°	36°	49°	60°	75°
S . . .	5·3	8·9	13·8	18·6	20·4	27·7	35·4	45·6

R. Lattey gave for the percentage solubility, S,

	0°	10°	20°	30°	50°	70°	90°	100°
S . .	3·26	4·31	5·61	7·17	11·02	15·88	21·74	25·04

The data are summarized in Fig. 357, and the solubility in mols per litre can be represented by $(99+2\cdot82\theta+0\cdot038\theta^2)\times10^{-4}$. F. R. Mallet prepared **potassium nickel trisulphate,** $K_2Ni_2(SO_4)_3$. H. Brintzinger and H. Osswald showed that in the sulphates of bivalent metals containing an excess of alkali or ammonium sulphates, the ions are of the type: $[Ni_2(SO_4)_4]''''$.

R. Bunsen and G. Kirchhoff prepared **rubidium nickel disulphate,** $Rb_2Ni(SO_4)_2.6H_2O$, from a mixed soln. of the component salts. A. Benrath's study of the ternary system: Rb_2SO_4–$NiSO_4$–H_2O is summarized in Fig. 358. The region of formation of the 1 : 1 : 6 salt is stippled, and Ni6α, Ni6β, and Ni7, respectively, denote the α- and β-hexahydrates, and the heptahydrate of nickel sulphate. F. R. Mallet prepared crystals of the anhydrous salt by fusing a mixture

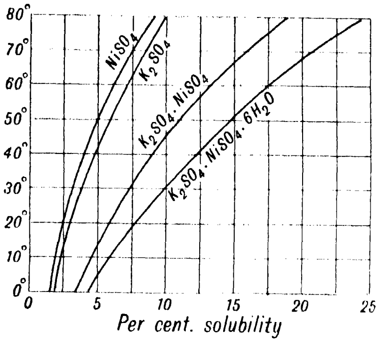


FIG. 357.—The Solubility of Potassium Nickel Sulphate.

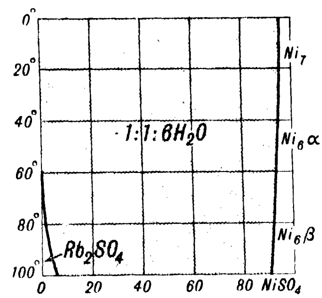


FIG. 358.—The Ternary System: Rb_2SO_4–$NiSO_4$–H_2O.

of theoretical proportions of the component salts. The dark green, tabular or prismatic, monoclinic crystals of the hexahydrate were found by A. E. H. Tutton to have the axial ratios $a:b:c=0{\cdot}7350:1:0{\cdot}5022$, and $\beta=106°\ 3'$. The optic axial angles are:

	Li-	C-	Na-	Tl-	F-light
$2E$ . . .	—	156° 3′	157° 0′	158° 5′	—
$2H_a$ . . .	73° 1′	72° 54′	72° 32′	72° 7′	71° 34′
$2H_o$ . . .	86° 15′	86° 7′	85° 46′	85° 31′	85° 15′
$2V_a$ . . .	82° 5′	82° 4′	82° 0′	81° 56′	81° 48′

The axial angle $2E$ increases by about 1·5° for 50° rise of temp. The topic axial ratios are $\chi:\psi:\omega=6{\cdot}1065:8{\cdot}3081:4{\cdot}1723$. The sp. gr. is 2·586 at 20°/4°, and the mol. vol. is 203·43. F. Ephraim and P. Wagner discussed the mol. vol. R. M. Caven and J. Ferguson found the vap. press., p mm., of the hexahydrate, to be:

	32·5°	40·1°	49·6°	58·3°	74·8°
p . . .	3·0	5·5	10·5	19·9	55·7

and $\log p=10{\cdot}563-2937T^{-1}-44{,}740T^{-2}$, as it passes to the dihydrate. The heat of hydration of the dihydrate is 14·4 Cals. per mol. of water vapour. According to A. E. H. Tutton, the refractive indices are:

	Li-	C-	Na-	Tl-	F-	G-light
α .	1·4868	1·4872	1·4895	1·4920	1·4949	1·4996
β .	1·4933	1·4937	1·4961	1·4987	1·5017	1·5062
γ .	1·5023	1·5027	1·5052	1·5078	1·5110	1·5156

where the mean value is 1·4969; and the double refraction of Na-light is $\gamma-\alpha=0{\cdot}0157$. The indices are lowered by about 0·015 for 50° rise of temp. The sp. refractions for the $C(H_\alpha)$- and the H_γ (near G)-rays, with the μ^2-formula, are, respectively, $\alpha=0{\cdot}1113$, and 0·1137; $\beta=0{\cdot}1125$, and 0·1149; and $\gamma=0{\cdot}1143$, and 0·1167; the mol. refractions, $\alpha=58{\cdot}53$, and 59·79; $\beta=59{\cdot}19$, and 60·46; and $\gamma=60{\cdot}10$, and 61·40; the mol. refractions with the μ-formula $\alpha=99{\cdot}11$, $\beta=100{\cdot}43$, and $\gamma=102{\cdot}26$—mean 100·60; the sp. dispersions with the μ^2-formula $\alpha=\beta=\gamma=0{\cdot}0024$; and the mol. dispersions, $\alpha=1{\cdot}26$, $\beta=1{\cdot}27$, and $\gamma=1{\cdot}30$. F. L. Perrot obtained the refractive indices $\alpha=1{\cdot}48963$, $\beta=1{\cdot}49666$, and $\gamma=1{\cdot}50582$ for Na-light. J. Locke found that a litre of water at 25° dissolves 59·8 grms. of the anhydrous salt.

R. Bunsen and G. Kirchhoff prepared **cæsium nickelous disulphate,** $Cs_2Ni(SO_4)_2.6H_2O$, from a mixed soln. of the component salts. F. R. Mallet prepared crystals of the anhydrous salt by fusing a mixture of the component salts in theoretical proportions. The bright green, monoclinic prisms of the *hexahydrate* were found by A. E. H. Tutton to have the axial ratios $a:b:c=0.7270:1:0.4984$, and $\beta=107° 2'$. The optic axial angle, $2V_a$, is:

	Li-	C-	Na-	Tl-	F-light
$2H_a$ . . .	78° 20′	78° 15′	78° 1′	77° 43′	77° 19′
$2H_o$ . . .	82° 59′	82° 55′	82° 27′	81° 59′	81° 11′
$2V_a$ . . .	87° 15′	87° 17′	87° 21′	87° 29′	87° 40′

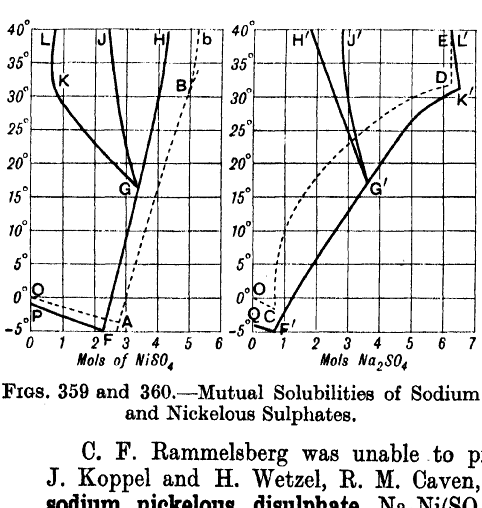
The topic axial ratios are $\chi:\psi:\omega=6.2097:8.5416:4.2572$. The sp. gr. is 2·872 at 20°/4°, and the mol. vol. 215·90. F. Ephraim and P. Wagner discussed the mol. vol. R. M. Caven and J. Ferguson found the vap. press., p mm., of the hexahydrate to be:

	35·0°	44·2°	48·7°	55·9°	65·7°	82·0°
p . . .	4·8	9·0	12·6	18·9	35·4	75·2

or $\log p=-1.730+4798T^{-1}-1{,}249{,}000^{-2}$, as it passes to the dihydrate. The heat of hydration of the dihydrate is 13·4 cals. per mol. of water vapour. According to A. E. H. Tutton, the refractive indices are:

	Li-	C-	Na-	Tl-	F-	G-light
α . . .	1·5061	1·5065	1·5087	1·5112	1·5146	1·5192
β . . .	1·5100	1·5104	1·5129	1·5154	1·5187	1·5235
γ . . .	1·5133	1·5137	1·5162	1·5189	1·5221	1·5266

where the mean value is 1·5126 for Na-light, and the double refraction is $\gamma-\alpha=0.0075$. The indices are lowered by about 0·0016 for 50° rise of temp. The sp. refractions for the $C(H_a)$- and the H_γ (near G)-rays, with the μ^2-formula, are, respectively, $\alpha=0.1035$, and 0·1057; $\beta=0.1042$, and 0·1064; $\gamma=0.1048$, and 0·1070; the mol. refractions, $\alpha=64.20$, and 65·55; $\beta=64.61$, and 66·00; and $\gamma=64.97$, and 66·34; the mol. refractions with the μ-formula, $\alpha=109.35$, $\beta=110.19$, and $\gamma=110.91$—mean 110·15; the sp. dispersions with the μ^2-formula are $\alpha=\beta=\gamma=0.0022$; and the mol. dispersions, $\alpha=1.35$, $\beta=1.39$, and $\gamma=1.37$. J. Locke found that a litre of water at 25° dissolves 255·8 grms. of the anhydrous salt.



FIGS. 359 and 360.—Mutual Solubilities of Sodium and Nickelous Sulphates.

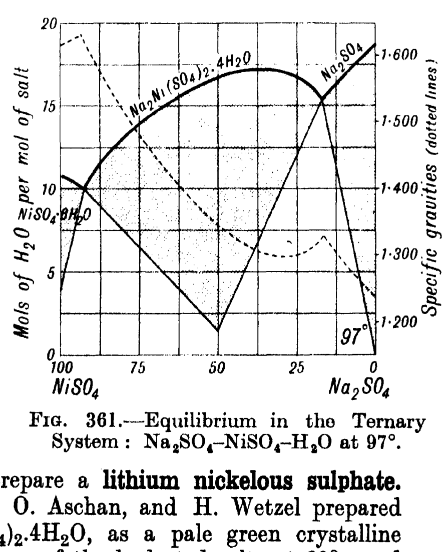


FIG. 361.—Equilibrium in the Ternary System: Na_2SO_4–$NiSO_4$–H_2O at 97°.

C. F. Rammelsberg was unable to prepare a **lithium nickelous sulphate.** J. Koppel and H. Wetzel, R. M. Caven, O. Aschan, and H. Wetzel prepared **sodium nickelous disulphate,** $Na_2Ni(SO_4)_2.4H_2O$, as a pale green crystalline powder, by melting together eq. proportions of the hydrated salts at 30°; and their observations on the system: Na_2SO_4–$NiSO_4$–H_2O, are summarized in Figs. 359 and 360. Corresponding soln. are designated with similar letters in both

diagrams, those without the dash refer to nickel sulphate; those with the dash to sodium sulphate. The curves *FG* and *F'G'* refer to the solubilities of mixtures of the component sulphates; *GJ* and *G'J'*, to the solubility of the complex salt $Na_2SO_4.NiSO_4.4H_2O$; *GH* and *G'H'*, to that of a mixture of the complex salt and nickel sulphate; *GKL* and *G'K'L'*, to that of a mixture of the complex salt and sodium sulphate; *OABb* to the solubility of nickel sulphate; *OCDE*, to the solubility of nickel sulphate; *A*, to the eutectic of $NiSO_4.7H_2O$ and ice; and *C*, to the eutectic of $Na_2SO_4.10H_2O$ and ice. The temp. of formation of the complex salt is 16·5°; the transformation temp. of decahydrated sodium sulphate in the presence of nickel sulphate is 31·8°; the eutectic with a mixture of the two hydrated sulphates is −5·1°. O. Aschan studied the formation of the salt. A. and H. Benrath examined the ternary system at 97°, and the following

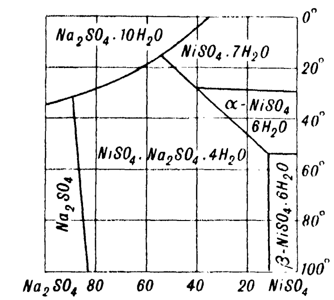


FIG. 362.—The Ternary System: Na_2SO_4–$NiSO_4$–H_2O.

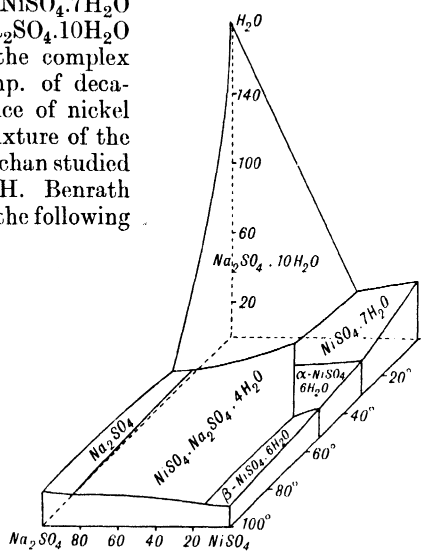


FIG. 363.—The Ternary System: Na_2SO_4–$NiSO_4$–H_2O.

is a selection of their results for the soln. in which the proportions of sodium and nickel sulphates are expressed in percentages by weight; *x* denotes the mol. proportion of $NiSO_4$ in the mixture; and *M*-, the number of mols. of water per mol. of salt:

$NiSO_4$.	0	2·30	6·49	16·33	33·73	43·18	43·40	45·57
Na_2SO_4	30·50	29·12	27·62	16·45	6·49	3·14	1·61	—
x . .	0	6·78	17·75	47·62	82·67	92·70	95·35	100·00
M .	18·56	17·32	15·49	16·87	12·59	9·90	10·37	10·69
	Na_2SO_4			$Na_2Ni(SO_4)_2.4H_2O$			$NiSO_4.6H_2O$	

The results are plotted in Fig. 361, where the dotted curve refers to the sp. gr. of the soln. A. Benrath's results at different temp. are summarized in Figs. 362 and 363. R. M. Caven and W. K. Gardner also studied the subject.

Some double salts of copper and nickel sulphates have been reported, but their existence as chemical individuals has not been established in view of the tendency of these salts to form isomorphous mixtures, or solid soln. A. Scott reported **copper nickelous trisulphate,** $CuSO_4.2NiSO_4.2H_2O$, to be formed by adding 130 c.c. of conc. sulphuric acid to a soln. of 100 grms. of heptahydrated nickel sulphate and 90 grms. of heptahydrated copper sulphate in 200 c.c. of water; washing the crystals two or three times with dil. sulphuric acid (1 : 1), and then with a mixture of dry ether and absolute alcohol; and drying over sulphuric acid, in vacuo. The pale yellowish-green *dihydrate* appeared homogeneous; A. Étard obtained the *trihydrate;* and H. Dufet, and L. de Boisbaudran, the *heptahydrate,* by the slow evaporation, at a low temp., of mixed soln. of the component salts. The monoclinic prisms had the axial ratios $a:b:c=1·7161:1:1·5480$, and $\beta=105° 12'$. C. von Hauer reported a *henicosihydrate* to be formed by spontane-

ously evaporating a mixed soln. of the component salts at ordinary temp. A. Étard obtained rose-coloured crystals of **copper nickelous dihydropentasulphate,** $2(CuSO_4.NiSO_4).H_2SO_4$, by heating in a sealed tube at 200°, a soln. of the mixed salts in the smallest possible proportion of water, and a large excess of conc. sulphuric acid.

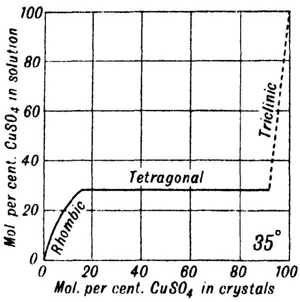


FIG. 364.—The Formation of Solid Solutions of Cupric and Nickel Sulphates at 35°.

According to E. Mitscherlich, when the proportion of copper sulphate in the soln. is comparatively small, the crystals of the solid which are deposited are monoclinic like heptahydrated ferrous sulphate, but when the proportion of copper sulphate in the soln. is large, triclinic crystals like pentahydrated cupric sulphate are formed. C. Weltzien added that the triclinic crystals have the molar ratio NiO : CuO=1·23, and the passage from the triclinic to the monoclinic form occurs when the proportion of NiO increases from 1·2 to 18·3 per cent. H. J. Brooke, and A. Fyfe examined the monoclinic crystals, and G. N. Wyrouboff made some observations on the subject. A. Fock obtained the following results, expressed in mol. percentages, at 35° :

		Rhombic		Tetragonal			
Solution	$CuSO_4$	1·57	7·69	11·66	16·92	25·63	27·90
	$NiSO_4$	98·43	92·31	88·34	83·08	74·37	72·10
Crystals	$CuSO_4$	0·35	2·12	4·77	6·52	13·88	18·77
	$NiSO_4$	99·65	97·88	95·23	93·48	82·12	81·23

It will be remembered—*vide supra*—that the rhombic sphenoids of heptahydrated nickel sulphate at room temp. pass into the tetragonal hexahydrate at 33° ; and above 60°, the crystals pass into the monoclinic form. Crystals with over 94·91 mol. per cent. of copper sulphate, and less than 5·09 per cent. of nickel sulphate were triclinic. These results are summarized in Fig. 364. At 67°, the crystals in the following systems were monoclinic :

Solution	$CuSO_4$	2·65	8·31	13·55	16·39	24·46
	$NiSO_4$	97·35	91·69	86·45	83·61	75·54
Crystals	$CuSO_4$	0·93	2·86	3·92	6·66	22·32
	$NiSO_4$	99·07	97·14	96·08	93·34	77·68

A. Recoura reported basic copper nickel sulphates to be formed by adding cupric hydroxide to aq. soln. of nickel sulphate ; with a cold soln., the blue flocculent precipitate had the composition $20CuO.NiSO_4.nH_2O$, and with a boiling soln., $16CuO.5NiSO_4.nH_2O$. A. Mailhe obtained by the action of a soln. of nickel sulphate on undried $4CuO.H_2O$, at 80°, **copper nickelous dioxysulphate,** $2CuO.NiSO_4.6H_2O$—with boiling soln., **copper nickelous trioxydisulphate,** $3CuO.2NiSO_4.10H_2O$, or, according to A. Werner, $Cu_2(OH)_4Cu : (OH)_2Ni(SO_4)_2Ni.7H_2O$. The decahydrate appears in green, rhombic plates. When in the cold soln., the *dodecahydrate* was formed in green, hexagonal plates. A. Fyfe, and W. A. Endriss studied these salts.

H. Vohl reported that the triple salt **ammonium copper nickel sulphate,** $2(NH_4)_2SO_4.CuSO_4.NiSO_4.12H_2O$, is formed from an aq. soln. of the component salts, but E. Barchet doubted its existence as a chemical individual, and regarded it as a solid soln. of the component salts. The ternary system : $CuSO_4$–$(NH_4)_2Ni(SO_4)_2$–H_2O, was studied by R. Lattey, and A. Fock. R. Lattey's results are summarized in Fig. 365. There is no evidence of the ternary salt. The area *EFGLK* is the saturation surface of the nickel double salt ; *GHL*, that of the copper ammonium double salt ; *ADKLH*, that of $CuSO_4.5H_2O$; *DBEK*, that of $NiSO_4.7H_2O$; and *FCG*, that of $(NH_4)_2SO_4$. D. Ostersetzer studied the solid soln. of ammonium copper sulphate and ammonium nickel sulphate. H. Vohl also reported **potassium copper nickel sulphate,** $2K_2SO_4.CuSO.NiSO_4.12H_2O$, to be formed in a similar manner; and A. Bette, from a mixed soln. of potassium copper

sulphate and potassium nickel sulphate. The pale green crystals are said to be stable in air; to give off water when heated; to dissolve in four times their weight of water; and to be insoluble in alcohol.

J. d'Ans observed that when the triple sulphate, $Ca_2MgK_2(SO_4)_4.2H_4O$, or polyhalite, is treated with a soln. of nickel sulphate, the magnesium is replaced by nickel to form **potassium calcium nickel sulphate,** $Ca_2NiK_2(SO_4)_4.2H_2O$, or *nickel-polyhalite.* S. V. Pickering obtained nickel oxysulphate mixed with very little calcium sulphate when a soln. of nickel sulphate is treated with calcium hydroxide. G. Klatzo reported the formation of **beryllium nickelous sulphate,** $(Be,Ni)SO_4.4H_2O$, from a neutral soln. of the component salts. The *tetrahydrate* furnishes well-formed, quadratic (tetragonal) crystals. Monoclinic crystals of the *hexahydrate* were also obtained, and rhombic crystals of the *heptahydrate.* A. N. Campbell and N. S. Yanick observed no evidence of the formation of a **calcium nickel sulphate** in their study of the system: $CaSO_4$–$NiSO_4$–H_2O at 45° to 90°. P. B. Sarkar and N. Ray prepared **ammonium beryllium nickelous fluosulphate,** $(NH_4)_2BeF_4.NiSO_4.6H_2O$; and also **potassium beryllium nickelous fluosulphate,** $K_2BeF_4.NiSO_4.6H_2O$. H. Schiff reported **magnesium nickelous sulphate,** $MgSO_4.3NiSO_4.28H_2O$, of sp. gr. 1·877, to be formed from a soln. of the component salts, but the product was probably a solid soln. of the two sulphates, $(Mg,Ni)SO_4.7H_2O$. E. Mitscherlich noted the isomorphism between nickel and magnesium sulphates; H. Dufet measured the indices of refraction of solid soln. of the two salts; and J. M. Thomson, the seeding of sat. soln. of magnesium sulphate with crystals of heptahydrated nickel sulphate. H. Dufet showed that there is a continuous series of rhombic sphenoidal crystals of solid soln. of the two salts, and the refractive indices all fall regularly between the values for the terminal members—heptahydrated magnesium sulphate 1·4554, and heptahydrated nickel sulphate 1·4893. H. Vohl reported triple salts: **ammonium magnesium nickelous sulphate,** $2(NH_4)_2SO_4.MgSO_4.NiSO_4.12H_2O$, in emerald-green crystals; and likewise also with **potassium magnesium nickelous sulphate,** $2K_2SO_4.MgSO_4.NiSO_4.12H_2O$.

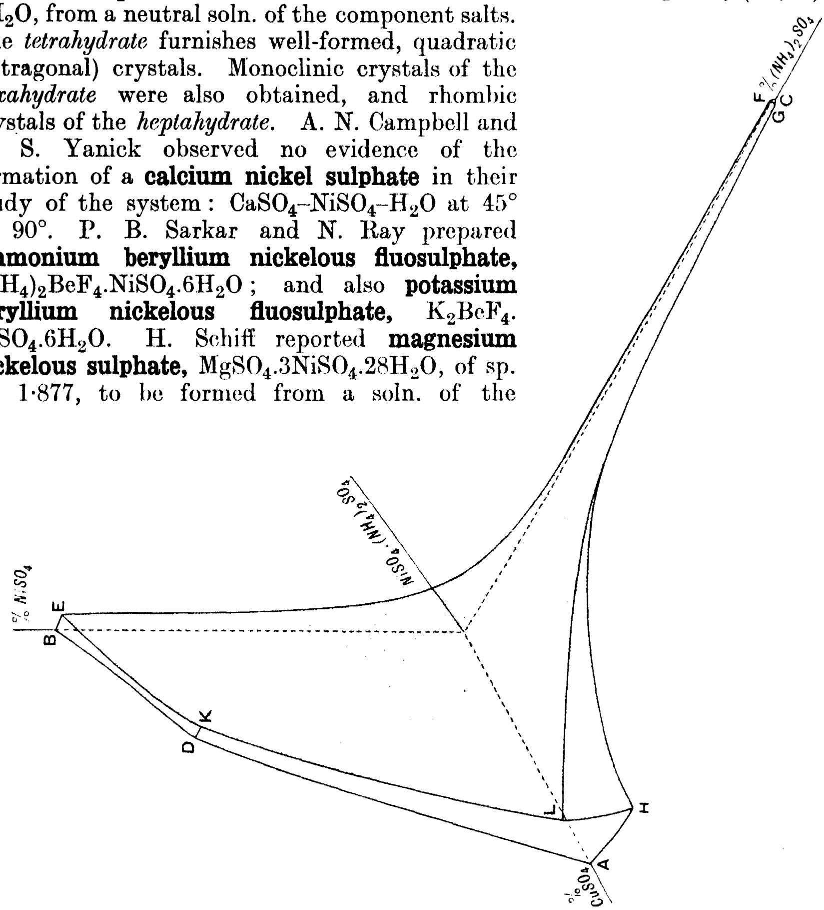


FIG. 365.—The System: $(NH_4)_2SO_4$–$NiSO_4$–$CuSO_4$–H_2O.

R. Tupputi reported **zinc nickelous sulphate,** $ZnSO_4.NiSO_4.13H_2O$, to be formed by crystallization from the soln. obtained by dissolving zinc in an acidic soln. of nickel sulphate. J. I. Pierre obtained the crystals from a soln. of the component salts. According to R. Tupputi, the pale green rhombic crystals have a sharp, astringent, metallic taste, and they readily effloresce in air. The crystals dissolve in three to four times their weight of cold water. A. Étard reported **zinc nickel hydrosulphate,** $2(ZnSO_4.NiSO_4).H_2SO_4$, to be formed by treating a conc. soln. of equimolar proportions of the component salts with cold, conc. sulphuric acid in a sealed tube at 200°. H. Vohl reported the triple salts : **ammonium zinc nickelous sulphate,** $2(NH_4)_2SO_4.ZnSO_4.NiSO_4.12H_2O$, in emerald-green, monoclinic, tabular and columnar crystals, which lose all their water at 180° ; and **potassium zinc nickelous sulphate,** $2K_2SO_4.ZnSO_4.NiSO_4.12H_2O$, also in emerald-green crystals. A. Scott reported the existence of a **cadmium nickelous sulphate.**

A. Étard reported **aluminium nickelous hydrosulphate,** $Al_2(SO_4)_3.2NiSO_4.H_2SO_4$, to be formed as a yellow, insoluble, crystalline mass, by heating a conc. soln. of equimolar proportions of aluminium and nickel sulphates with conc. sulphuric acid in a sealed tube at 200°. R. M. Caven and T. C. Mitchell observed no evidence of the formation of a complex **aluminium nickel sulphate** at 30°. Expressing solubility concentrations in grams per 100 grms. of soln., they found :

$Al_2(SO_4)_3$.	28·86	25·82	21·95	21·30	20·79	8·70	5·29	0
$NiSO_4$.	0	4·74	10·87	12·91	13·29	22·56	26·03	30·77
Solid phase		$Al_2(SO_4)_3.nH_2O$				$NiSO_4.nH_2O$		

G. Werther prepared **thallous nickelous disulphate,** $Tl_2Ni(SO_4)_2.6H_2O$, from a soln. of the component salts. A. Benrath's study of the system : Tl_2SO_4–$NiSO_4$–H_2O is summarized in Fig. 366, the region of formation of the 1 : 1 : 6 double salt is stippled ; $Ni_6\alpha$, $Ni_6\beta$, and Ni_7, respectively, denote the α- and β-hexahydrates, and the heptahydrate of nickel sulphate. F. R. Mallet prepared crystals of the anhydrous salt by fusing a mixture of theoretical proportions of the component salts. The bright green crystals of the hexahydrate were found by G. Werther to be monoclinic prisms with the axial ratios $a:b:c=0·743:1:0·499$, and $\beta=106°\ 39'$. Observations were also made by C. F. Rammelsberg ; and A. E. H. Tutton gave 0·7404 : 1 : 0·4997, and $\beta=106°\ 23'$; and for the optic axial angles :

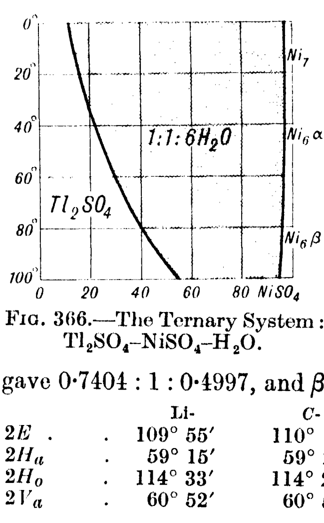


Fig. 366.—The Ternary System : Tl_2SO_4–$NiSO_4$–H_2O.

	Li-	C-	Na-	Tl-	Cd-	*F*-light
$2E$.	109° 55′	110° 5′	112° 3′	113° 55′	115° 20′	117° 5′
$2H_a$.	59° 15′	59° 20′	59° 42′	60° 7′	60° 22′	60° 38′
$2H_o$.	114° 33′	114° 22′	113° 9′	111° 56′	111° 9′	110° 17′
$2V_a$.	60° 52′	60° 58′	61° 37′	62° 17′	62° 43′	63° 11′

The sp. gr. is 3·770 at 20°/4° ; the mol. vol., 201·97 ; the topic axial ratios $\chi:\psi:\omega=6·1354:8·2865:4·1408$; and the refractive indices :

	Li-	*C*-	Na-	Tl-	Cd-	*F*-	*G*-light
α . . .	1·5944	1·5990	1·6024	1·6063	1·6086	1·6115	1·6191
β . . .	1·6144	1·6150	1·6183	1·6222	1·6252	1·6280	1·6385
γ . . .	1·6184	1·6190	1·6224	1·6264	1·6290	1·6324	1·6400

The mean value for Na-light is 1·6144, and the double refraction $\gamma-\alpha=0·0200$. The values of β, corrected to a vacuum, are reproduced by $\beta=1·6041+402{,}008\lambda^{-2}+3{,}637{,}200{,}000{,}000\lambda^{-4}+\ldots$; and the values of α are reproduced if the constant 1·6041 is diminished by 0·0160 and the values of γ if 1·6041 be increased to 1·6082. The sp. refractions for the μ^2-formula for the $C(H_\alpha)$- and the H_γ (near G)-rays, are, respectively, $\alpha=0·0906$, and 0·0931 ; $\beta=0·0926$, and 0·0950 ; and $\gamma=0·0931$, and

0·0956; the mol. refractions, α=69·00, and 70·86; β=70·48, and 72·37; and γ=70·85, and 72·76; the mol. refractions with the μ-formula are α=120·98, β=124·21, and γ=125·02—mean 123·40; the sp. dispersions with the μ^2-formula, α=0·0025, β=0·0024, and γ=0·0025; and the mol. dispersions, α=1·86, β=1·89, and γ=1·91. The crystals were found by G. Werther to be stable in air, and to lose their water of hydration at 120°; J. F. Willem found virtually no water is lost at 100°, and nearly all at 150°. According to G. Werther, the dehydrated salt may be heated to 300° without decomposition; it melts below a red-heat; and decomposes at a bright red-heat. The dehydrated salt is yellow when cold, and orange-red when melted. The salt can be recrystallized from aq. soln. J. Locke found that at 25° a litre of water dissolves 46·1 grms. of the anhydrous salt.

A. Étard reported **chromic nickelous hydrosulphate,** $Cr_2(SO_4)_3.NiSO_4.2H_2SO_4.3H_2O$, to be formed by heating a conc. soln. of equimolar parts of the component salts with a large excess of conc. sulphuric acid in a sealed tube at 200°. The greenish-yellow crystals are insoluble in water.

H. Vohl reported the triple salts: **ammonium manganous nickelous sulphate,** $2(NH_4)_2SO_4.MnSO_4.NiSO_4.12H_2O$, in emerald-green crystals which lose water at 180°; and **potassium manganous nickelous sulphate,** $2K_2SO_4.MnSO_4.NiSO_4.12H_2O$.

H. F. Link reported **ferrous nickelous sulphate** to be formed in green crystals from a soln. of the component salts. The rhombic crystals crumble to a yellow powder on exposure to air. J. W. Retgers studied the solid soln. formed by the heptahydrated ferrous and nickelous sulphates. Rhombic crystals are formed with 0 to 21·10 per cent. $FeSO_4.7H_2O$, and with 100 to 78·90 per cent. $NiSO_4.7H_2O$; and monoclinic crystals with 49·63 to 100 per cent. $FeSO_4.7H_2O$, and 50·37 to 0 per cent. $NiSO_4.7H_2O$. A. Étard also prepared **ferrous nickelous hydrosulphate,** $2FeSO_4.NiSO_4.H_2SO_4$, by heating a conc. soln. of equimolar parts of the component salts with an excess of conc. sulphuric acid in a sealed tube at 200°. H. Vohl reported **ammonium ferrous nickelous sulphate,** $2(NH_4)_2SO_4.FeSO_4.NiSO_4.12H_2O$, in emerald-green crystals; and likewise **potassium ferrous nickelous sulphate,** $2K_2SO_4.FeSO_4.NiSO_4.12H_2O$. A. Étard prepared **ferric nickelous hydrosulphate,** $Fe_2(SO_4)_3.NiSO_4.2H_2SO_4$, by heating a conc. soln. of the component salts with a large excess of conc. sulphuric acid in a sealed tube at 200°. The yellow crystals are insoluble in water.

A. Scott obtained **cobaltous nickelous sulphate,** $CoSO_4.NiSO_4.2H_2O$, in pink crystals, by adding conc. sulphuric acid to a soln. of eq. proportions of the com-

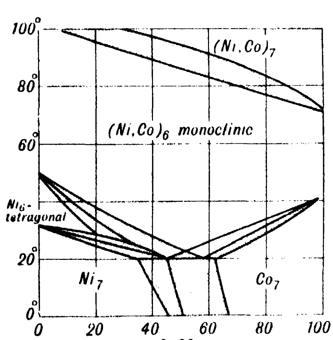


FIG. 367.—xt-Diagram.

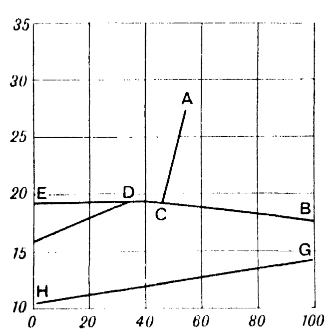


FIG. 368.—xm-Diagram.

ponent salts. According to G. Brügelmann, when equal vols. of cold, sat. soln. of cobalt chloride and nickel sulphate are mixed, and allowed to evaporate spontaneously, the crystals contain sulphates of both metals, whilst the chlorides remain in soln. A. Benrath and co-workers studied the system of solid soln. and obtained the results summarized in Figs. 367 and 368. In Fig. 368, *A* denotes the hepta-

hydrates of cobalt and nickel with x, 53·6 ; m, 26·9 at 0° ; B, Co_7–Co_6, with x, 100 ; m, 17·5, at 41·5° ; E, Ni_7–Ni_6(monoclinic), with x, 0 ; m, 19·4, at 31·5° ; F, Ni_6(monoclinic)–Ni_6(tetragonal), x, 0 ; m, 16·3, at 52·5° ; G, Co_6–Co_1, x, 100 ; m, 13·8 at 71·0° ; H, Ni_6(tetragonal)–Ni_1, with x, 0 ; m, 10·6, at 103° ; C, Co_7–Ni_7–$(Co,Ni)_6$(tetragonal), x, 46·5 ; m, 19·5, at 21° ; D, Ni_7–Ni_6(monoclinic)–$(Co,Ni)_6$(tetragonal), x, 35 ; m, 19·5, at 26°. H. Vohl obtained **ammonium cobaltous nickelous sulphate,** $2(NH_4)_2SO_4.CoSO_4.NiSO_4.12H_2O$, in dirty greenish-grey columns and plates; and **potassium cobaltous nickelous sulphate,** $2K_2SO_4.CoSO_4.NiSO_4.12H_2O$, in dirty greyish-green columns and plates. J. M. Thomson could find no justification for regarding those products as chemical individuals ; they have the character of solid soln.

S. R. Benedict [3] reported **nickelic sulphate,** presumably $Ni_2(SO_4)_3$, to be formed in soln. when freshly-precipitated nickelic hydroxide is treated with a nearly sat. soln. of potassium hydrosulphate. The soln. is so powerful an oxidizing agent that he supposed it to contain either a simple or complex nickelic sulphate—*vide supra*, nickelic oxide. As indicated in connection with the electrolysis of ammonium nickelous sulphate, W. Pfanhauser assumed that with higher voltages, nickelic sulphate is formed momentarily at the anode, and immediately hydrolyzed to nickelic hydroxide. C. Tubandt and W. Riedel found that the soln. of the alleged nickelic sulphate, obtained by S. R. Benedict, is really a soln. of nickelous sulphate in permonosulphuric acid, and that the red colour which S. R. Benedict observed is due to the presence of manganese oxidized to permanganate by the nickelic oxide. They concluded that all attempts to prepare a nickelic salt are *völlig ergebnislos*, and must be regarded as *aussichtlos*. R. H. Weber discussed the magnetic properties.

P. C. Ray and P. B. Sarkar [4] prepared monoclinic crystals of **ammonium nickel sulphatofluoberyllate,** $(NH_4)_2BeF_4.NiSO_4.6H_2O$, and also **potassium nickel sulphatofluoberyllate,** $K_2BeF_4.NiSO_4.6H_2O$, each of which is a member of an isomorphous series with Co, Fe, Mn, Cd, Zn, and Mg in place of Ni. The salts were studied by H. Seifert.

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§ 19. Nickel Carbonates

H. de Sénarmont[1] prepared anhydrous **nickel carbonate**, $NiCO_3$, by heating an aq. soln. of nickel chloride with calcium carbonate in a sealed tube for 18 hrs. at 150°; and also from a soln. of nickel chloride and sodium carbonate saturated with carbon dioxide, heated in a sealed tube at 140°. J. Krustinsons found that the carbonate so prepared contains some nickel chloride; and analogously with cobalt nitrate. J. P. Laroche and J. P. Paat also obtained it by treating the oxalate with potash-lye or soda-lye in sat. soln. at 100°. A. Ferrari and C. Colla could not prepare the normal carbonate. M. Sergeeff said that precipitation is best effected at the b.p. with an excess of sodium carbonate. T. Nanty obtained the *trihydrate*, $NiCO_3.3H_2O$, by adding a soln. of potassium hydrocarbonate to a soln. of nickel chloride at ordinary temp.—*vide infra*, potassium nickel carbonate. H. St. C. Deville reported the *hexahydrate*, $NiCO_3.6H_2O$, to be formed in rhombohedral or monoclinic prisms by the action of sodium or ammonium hydrocarbonate on a soln. of nickel nitrate. It is difficult to wash the soda away from the precipitate when sodium hydrocarbonate is employed. E. Müller and A. Luber found that an aq. soln. of carbon dioxide reacts with nickel reversibly and for a given temp. and press., the conc. of the dissolved metal is accurately reproducible.

Nickel is dissolved as **nickel hydrocarbonate,** $Ni(HCO_3)_2$, which cannot be obtained in the solid form, but crystalline $NiCO_3$, and $NiCO_3.6H_2O$ can be prepared. The hexahydrate readily loses its water of hydration. R. A. Fereday studied the magnetic susceptibility of the carbonate.

J. L. Proust, H. Rose, and H. Moissan found that when the carbonate is heated in air, it forms some nickelic oxide. B. Srebrow found that the decomposition temperature is lowered by the presence of oxides of Mn, Fe, Co, Ni, and Mg. K. K. Kelley and C. T. Anderson studied the subject. H. de Sénarmont observed that the anhydrous carbonate furnishes pale green, transparent, microscopic rhombohedra. It is not attacked in the cold by conc. hydrochloric acid. N. C. Nag found that in the presence of sodium acetate, bromine forms a brownish-red soln. which, when boiled, deposits a violet precipitate of nickel dioxide. According to J. Gibson, if excess of sodium carbonate is added to a soln. of a nickel salt, the resulting mixture behaves differently on addition of bromine, according to the quantity of bromine added. If a large excess of bromine is added, part of the nickel goes into soln., part remains undissolved as pale-green carbonate; if a smaller proportion of bromine is added, so as to have excess of sodium carbonate, the nickel is completely converted into peroxide. C. F. Rammelsberg observed that the carbonate dissolves in a soln. of paraperiodic acid forming a green liquid. L. R. von Fellenberg found that when heated with sulphur and potassium carbonate, nickel disulphide is formed. H. A. Frasch found that the carbonate reacts with ammonia and alkali chlorides in accord with the equation: $NiCO_3+6NH_3+2NaCl=Ni(NH_3)_6Cl_2+Na_2CO_3$. L. Santi observed that the carbonate is decomposed by an aq. soln. of ammonium chloride, carbon dioxide and ammonia are evolved, and a soln. of nickel chloride remains. R. Emerson was unable to confirm the photosynthetic activity of nickel carbonate in its action on carbon dioxide for the production of oxygen and carbohydrates reported by E. C. C. Baly and co-workers. H. Goldschmidt and K. L. Syngros passed air through a soln. of nickel chloride and hydroxylamine hydrochloride and obtained yellowish-green **nickel hydroxylamine hydroxycarbonate,** $2Ni(OH)_2.4NiCO_3.5NH_2OH.7H_2O$, which explodes when heated; the filtrate from this salt, when exposed to the continued action of air, deposits a pale green salt, $2Ni(OH)_2.4NiCO_3.6NH_2OH.6H_2O$. The mineral **zaratite,** $NiCO_3.2Ni(OH)_2.4H_2O$, was synthesized by M. Fenoglio by the action of a soln. of nickel chloride on nesquehonite, $MgCO_3.3H_2O$. The sp. gr. is 2·664, and the index of refraction of the isotropic salt is 1·58 to 1·60.

The crystals of anhydrous nickel carbonate are insoluble in nitric acid. N. R. Dhar and co-workers, G. Rao and N. R. Dhar, and G. MacKinney studied the catalytic action of the carbonate on the photoreduction of carbon dioxide to form aldehyde. G. T. Morgan and F. H. Burstall prepared **nickelous tris-$\alpha\alpha'$-dipyridylcarbonate,** $[Ni(C_{10}H_8N_2)_3]CO_3.6H_2O$, by passing carbon dioxide through a soln. of nickelous tris-$\alpha\alpha'$-dipyridylhydroxide. N. A. Yajnik and F. C. Trehana studied the action of the carbonate on the photochemical reduction of sugars.

F. Ageno and E. Valla found that a litre of water at 25° dissolves 0·0925 grm. of nickel carbonate; and the hydrolysis in the aq. soln. in an atm. of carbon dioxide is 98·92 per cent. J. L. Proust noted that both nickel oxide and hydroxide absorb carbon dioxide from atm. air and thereby acquire a green colour. P. N. Raikow found that an excess of carbon dioxide converts nickel hydroxide into a nickel hydrocarbonate, $Ni_3H_2(CO_3)_4$. This salt is fairly soluble in a soln. saturated with carbon dioxide, but nickel carbonate is deposited as the gas escapes from the soln.

Nickel carbonate readily forms basic salts. This might be anticipated from the ready hydrolysis of the salt. In most cases it is highly probable that the products which have been reported are equivalent to stages selected by chance in the process of hydrolysis. According to P. C. L. Thorne, a soln. of nickel carbonyl in toluene deposits a basic carbonate on exposure to air. B. Sillimann described what he called *hydrate of nickel,* and *emerald nickel* as an occurrence on the chromite

at Texas, Pennsylvania; A. Casares, as an incrustation on some nickeliferous magnetite near Cape Hortegal, Galicia, Spain; and other occurrences were reported by W. W. Beck, O. B. Böggild, R. L. Codazzi, J. D. Dana, T. H. Garrett, J. G. Goodchild, R. P. Greg and W. G. Lettsom, L. L. Iwanoff, P. W. Jeremejeff, R. D. O. Johnson, T. Petersen, W. F. Petterd, A. Raimondi, E. Weinschenk, and V. R. von Zepharovich. According to E. Cohen, an incrustation of zaratite was observed on a meteorite from Dnieprowsk. Analyses were reported by R. D. Thomson, B. Silliman, J. L. Smith and G. J. Brush, and C. F. Rammelsberg; they indicate that the composition approximates **nickel tetrahydroxycarbonate,** $NiCO_3.2Ni(OH)_2.4H_2O$, or $3NiO.CO_2.6H_2O$. P. Groth represented the composition by the formula $(NiOH)_2CO_3.Ni(OH)_2.4H_2O$. W. Feitknecht found that the space-lattice of $NiCO_3.3Ni(OH)_2$ corresponds with alternate layers of normal salt and hydroxide. M. Fenoglio found the mineral is isotropic, and the cubic lattice has a=6·15 A., and there is 1 mol. per unit cell. The sp. gr. is 2·649. G. A. Kenngott proposed to call the mineral *texasite*, but the prior suggestion of A. Casares to call it **zaratite**—after S. Zarate of Spain—has been adopted. Zaratite occurs as an incrustation or in small stalactitic or mammillary masses, sometimes prismatic with rounded summits; and sometimes massive and compact. Zaratite is translucent or transparent, amorphous and isotropic, but W. W. Beck said that the zaratite from Ufa, Russia, showed signs of a crystalline structure in polarized light. The colour is emerald-green; the streak is a paler colour. The sp. gr. ranges from 2·57 to 2·69; and the hardness, 3·0 to 3·25. E. S. Larsen found the index of refraction 1·56 to 1·61 in Na-light. F. Slavik gave 1·565 to 1·566; and A. Pelloux, 1·56. The birefringence is feeble. It readily dissolves with effervescence in hot, dil. hydrochloric acid.

Alkali carbonates precipitate from soln. of nickel salts pale apple-green flecks, which, after washing, and drying, sometimes form a loose, earthy, pale green mass, and sometimes, particularly after washing with boiling water, a compact, dark green mass with a conchoidal, waxy fracture. The precipitate is always basic, and the composition depends on the precipitant—alkali carbonate or hydrocarbonate—on the composition and temp. of the mixture, on the temp. of the wash-water, and the amount of washing which is made. This is shown by the observations of R. Weber, H. Rose, P. Berthier, and J. Lefort.

According to J. Setterberg, the ratio $NiO : CO_2 : H_2O$ is 1 : 2·2124 : 2·331, when precipitated by potassium hydrocarbonate and dried in air; 1 : 1·441 : 2·973, when precipitated by potassium carbonate and dried in air; 1 : 1·079 : 0·960, when precipitated by potassium hydrocarbonate from a boiling conc. soln. of nickel chloride; 1 : 0·362 : 1·338, when a dil. soln. of nickel salt is treated with a slight excess of potassium carbonate and washed with cold water, if washed with hot water the ratio is 1 : 0·357 : 1·184; 1 : 0·734 : 0·759, when precipitated from a moderately conc., boiling soln. by an excess of potassium carbonate and dried in air; 1 : 0·179 : 0·694, when treated in the same way but with more dil. soln., washed with boiling water, and dried in air; and 1 : 0·225 : 1·496, when precipitated from a moderately conc. soln. by potassium carbonate, and dried in air.

H. Rose observed that the basic carbonate is insoluble in water, or carbonic acid; it is soluble in acids, and in soln. of ammonium carbonate, or potassium cyanide, and in warm soln. of ammonium chloride, but sparingly soluble in soln. of sodium carbonate. J. Spiller noticed that the presence of sodium citrate prevents the precipitation of the basic carbonate. D. Strömholm studied the action of soln. containing sodium carbonate, hydrocarbonate, or hydroxide in varying proportions on soln. of nickel salts, after equilibrium has been attained, and the results indicated the probable existence of a basic salt with the zaratite ratio $3NiO.CO_2.nH_2O$. T. Nanty also studied the reversible reaction between potassium hydrocarbonate and a nickel salt in aq. soln. I. I. Wanin and A. A. Tschernoyarova studied the action on benzal chloride.

According to R. Tupputi, nickel carbonate dissolves in an aq. soln. of ammonium carbonate, forming a greenish-blue soln., and when this soln., or an ammoniacal soln. of nickel hydroxide is exposed to air, pale green, insoluble flakes of **ammo-**

nium nickel carbonate, possibly $(NH_4)HCO_3.NiCO_3.4H_2O$, are deposited. H. St. C. Deville found this to be the composition of the precipitate obtained by adding an excess of ammonium hydrocarbonate to a soln. of nickel nitrate, and allowing the mixture to stand for some time. The apple-green crystals lose water in an evacuated desiccator.

Nickel oxide does not dissolve in fused sodium carbonate before the blowpipe flame. H. Rose observed that when a soln. of nickel nitrate is treated with an excess of sodium hydrocarbonate, $Na_2CO_3.2NaHCO_3$, a pale green precipitate containing about 3·6 to 8·8 per cent. of sodium is obtained. In the opinion of H. St. C. Deville, this product is not a chemical individual, but he obtained **sodium nickel carbonate,** $Na_2CO_3.NiCO_3.10H_2O$, by gradually mixing a soln. of nickel nitrate with a conc. soln. of sodium hydrocarbonate so that the latter is always in excess. The flocculent precipitate soon forms small, grass-green crystals approximating to the rhombohedral form. The salt $Na_2CO_3.NiCO_3.4H_2O$ was also prepared by M. P. Applebey and K. W. Lane. By similarly treating nickel nitrate with potassium hydrocarbonate, $K_2CO_3.2KHCO_3$, he obtained apple-green, acicular crystals of **potassium nickel carbonate,** $K_2CO_3.NiCO_3.4H_2O$; W. C. Reynolds obtained the same compound by cooling a hot soln. of a nickel salt and potassium carbonate; and by using potassium hydrocarbonate, $KHCO_3$, as precipitant, H. Rose, and H. St. C. Deville obtained dark green, rhombic prisms of **potassium nickel hydrocarbonate,** $KHCO_3.NiCO_3.4H_2O$. This salt is decomposed by water, and it was therefore washed with a soln. of potassium hydrocarbonate and dried between bibulous paper, or on a porous tile. It loses about 32·7 per cent. in weight at 100°, and when calcined forms nickel oxide. This salt was also prepared by M. P. Applebey and K. W. Lane. T. Nanty found that the composition of the precipitate produced at ordinary temp. by potassium hydrocarbonate and a soln. of a nickel salt depends solely on the conc. of the two salts. On the one hand, the trihydrate, $NiCO_3.3H_2O$, may be precipitated, or else $NiCO_3.KHCO_3.4H_2O$, or a mixture of the two.

O. F. Wiede and K. A. Hofmann [2] prepared **nickel triamminothiocarbonate,** $NiCS_3.3NH_3$, by gently warming a mixture of nickelous hydroxide, ammonia, and carbon disulphide. It crystallizes in transparent, ruby-red needles, is sparingly soluble in water, but easily in sodium hydroxide with an intense, yellowish-red coloration, and, when heated, gives off carbon disulphide. On exposure to the air, it gives off part of the ammonia and carbon disulphide.

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§ 20. Nickel Nitrate

An aq. soln. of **nickelous nitrate,** $Ni(NO_3)_2$, is formed by dissolving the metal, the oxide, the hydroxide, or the carbonate in nitric acid; evaporation of the aq. soln. furnishes the hydrated salt, and it is then possible to dehydrate the product to yield the yellow anhydrous salt. These facts were known to T. Bergman,[1] and J. L. Proust. The dehydration of the hydrated nitrate by heat yields a basic salt, or oxide. A. Guntz and F. Martin said that the anhydrous nitrate is obtained by the action of nitric anhydride, or of a soln. of this anhydride in nitric acid, on the hydrated salts. Anhydrous nickel nitrate is a pale greenish-yellow powder; and

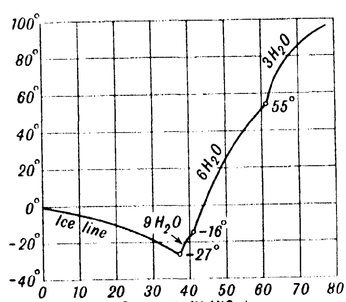

FIG. 369.—The Solubility of Nickelous Nitrate.

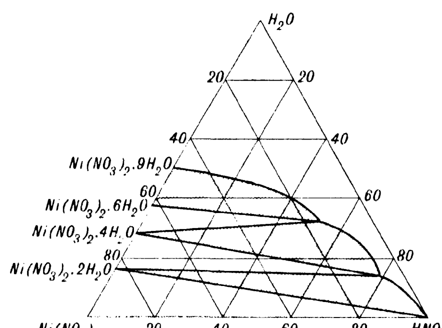

FIG. 370.—The Ternary System: $Ni(NO_3)_2$–HNO_3–H_2O at 25°.

the aq. soln. is green. R. Tupputi said that at ordinary temp. the salt dissolves in twice its weight of water. The percentage **solubility,** *S*, of the salt in water, was measured by R. Funk, and F. Mylius and R. Funk.

	−7·4°	−20°	−27°	−20°	−16°	0°	40°	55°	70°	95°
S . . .	18·0	34·7	38·7	39·7	40·8	44·3	54·8	61·1	63·9	77·2
	Ice line			$Ni(NO_3)_2.9H_2O$		$Ni(NO_3)_2.6H_2O$			$Ni(NO_3)_2.3H_2O$	

The datum for $-7\cdot4°$ is by F. Rüdorff, and the transition temp. were obtained by interpolation. The **eutectic temperature** is thus at $-27°$, with the solid phases ice and the *enneahydrate*, $Ni(NO_3)_2.9H_2O$; the transition temperature from the enneahydrate to the *hexahydrate*, $Ni(NO_3)_2.6H_2O$, is near $-16°$; and the transition temp. from the hexahydrate to the trihydrate, $Ni(NO_3)_2.3H_2O$, is near 55°. J. M. Ordway reported an unstable form of the hexahydrate with a solubility 62·8 at 56·7°. The ranges of stability of the hydrates are indicated in Fig. 369. The conc. aq. soln. at ordinary temp. deposits crystals of the hexahydrate. Observations were also made by A. Sieverts and L. Schreiner, and I. Schumpelt. A. Sieverts and L. Schreiner studied the ternary system $Ni(NO_3)_2$–HNO_3–H_2O at 25°, and the results are summarized in Fig. 370. The range of existence of the *enneahydrate*, the *hexahydrate*, the *tetrahydrate*, and the *dihydrate* are indicated.

The **crystals** of the hexahydrate are emerald-green plates, and, according to J. C. G. de Marignac, they belong to the monoclinic system, and have the axial ratios $a:b:c=0\cdot5834:1:0\cdot9567$, and $\beta=101°\ 26'$. The crystals were also discussed by C. F. Rammelsberg. J. Markowska studied the solid soln. formed with hexahydrated magnesium nitrate. P. A. Favre and C. A. Valson gave 1·993 for the **specific gravity** of the hexahydrate ; F. W. Clarke gave 2·065 at 14° and 2·037 at 22° ; and J. Garcia-Viana and E. Moles, 2·002 at 25°/4°. The sp. gr. of aq. soln. at 17·5°, found by B. Franz for soln.:

$Ni(NO_3)_2$	5	10	15	20	25	30	35	40 per cent.
Sp. gr.	1·0463	1·0903	1·1375	1·1935	1·2534	1·3193	1·3896	1·4667

J. Wagner gave for N-, $0\cdot5N$-, $0\cdot25N$-, and $0\cdot125N$-$Ni(NO_3)_2$, at 25°, the respective sp. gr. 1·0755, 1·0381, 1·0192, and 1·0096. H. C. Jones and J. N. Pearce gave for soln. with M-mols of salt per litre, at 20° :

M	0·01	0·05	0·10	0·50	1·0	1·5	2·0
Sp. gr.	1·001521	1·007792	1·015307	1·07611	1·14562	1·22134	1·29459

Measurements were made by G. T. Gerlach, A. Heydweiller, A. Bromer, B. Franz, and I. Traube. The *International Critical Tables* gave for different temp.,

$Ni(NO_3)_2$		1	6	10	16	20	25	30	35 per cent.
Sp. gr.	18°	1·0070	1·0508	1·0882	1·1484	1·1914	1·2493	1·3114	1·3777
	20°	1·0065	1·0503	1·0877	1·1480	1·1910	1·2490	1·3110	1·3770
	25°	1·0055	1·0494	1·0850	1·1430	1·1860	1·2430	1·3040	1·3700

The subject was discussed by J. A. Groshans. G. Dreyer gave for the lowering of the temp. of **maximum density** of water, 3·96°, by p per cent. soln. of $Ni(NO_3)_2$,

p	0·182	0·370	0·758	1·556	1·593
Lowering	0·28°	0·57°	1·15°	2·42°	2·49°

According to P. A. Favre and C. A. Valson, for soln. with N-gram-equivalents of $Ni(NO_3)_2$ per litre at 24·4°, the sp. gr., the vol., v, obtained by dividing the total weight of salt and water by the sp. gr., and δv, the increase in vol. produced by successive additions of an eq. of the salt, are:

		1	2	3	4	5	6
$Ni(NO_3)_2$	Sp. gr.	1·073	1·141	1·205	1·266	1·324	1·378
	Volume	1017	1036	1057	1079	1101	1124 c.c.
	Vol. Incr.	17	19	21	22	22	23 c.c.
$Ni(NO_3)_2.6H_2O$	Sp. gr.	1·069	1·128	1·179	1·224	1·264	1·299
	Volume	1071	1144	1218	1292	1367	1442 c.c.
	Vol. Incr.	71	73	74	74	75	75 c.c.

G. Tammann studied the **inner pressure** of soln. J. Wagner gave for the **viscosities** of N-, $0\cdot5N$-, $0\cdot25N$-, and $0\cdot125N$-soln., at 25°, respectively, 1·1800, 1·0840, 1·0422, and 1·0195 (water unity). E. Rona studied the **diffusion** of nickel nitrate in aq. soln. at 18°, and found for the diffusion coeff., D, in $0\cdot068N$-aq. soln. and $0\cdot0413N$-HNO_3, in $0\cdot0413N$-aq. soln. and $0\cdot1N$-HNO_3 ; and $0\cdot0108N$-aq. soln. and

0101N-HNO_3, respectively, 0·802, 0·646, and 0·719. The hydrate gives off moisture when heated. M. A. Rakuzin studied the efflorescence of the crystals—*vide infra.* According to J. L. Proust, in the **thermal decomposition** of hydrated nickel nitrate, a basic nitrate, and later, nickel oxide are formed; and J. J. Berzelius added that some nickel peroxide may be formed. A. Guntz and F. Martin observed that the anhydrous salt begins to evolve nitrous fumes at 105° to 110°; and J. Garcia-Viana and E. Moles added that the loss of nitric acid occurs when the dehydration is carried beyond the loss of 4 mols. J. C. G. de Marignac gave for the **specific heat,** between 24° and 55°, of aq. soln. with 25, 50, and 200 mols. of water per mol. of salt, respectively, 0·7171, 0·8228, and 0·9409. The subject was discussed by K. Jauch, and N. de Kolossowsky. H. Lescœur found that the **vapour pressure** of a sat. soln. of nickel nitrite at 20° is about 8·5 mm. G. Tammann measured the lowering of the vap. press. of water by nickel nitrate, and found for soln. with 10·15, 40·16, and 80·25 grms. of the anhydrous salt per 100 grms. of water at 100°, respectively, 18·2, 102·3, and 255·8 mm. H. C. Jones and co-workers found the **lowering of the freezing point** of water, $\delta\theta$, by the dissolution of C grms. of the anhydrous nitrate per 100 grms. of water, to be:

C . . .	0·1827	1·370	4·568	13·70	27·41
$\delta\theta$ (fall) . .	0·1299°	0·3644°	1·251°	4·213°	10·576°

Observations were made by F. Rüdorff, C. Dieterici, and F. Mylius and R. Funk, Fig. 369. E. N. Gapon studied some relations of the **boiling point** of aq. soln. of the nitrate. J. M. Ordway found that the b.p. of the sat. aq. soln. is 136·7°, and that with a continuous boiling the soln. remains clear until less than 3 mols. of water are present per mol. of anhydrous salt, and then some nitrate is decomposed. He also gave 56·7° for the **melting point** of the hexahydrate. R. Funk, and W. A. Tilden discussed this subject. According to J. G. Viana and E. Moles, in the dehydration of the hexahydrate, nitric acid is lost only after 4 mols. of water have been given off to form a salt of orthonitric acid.

According to J. Thomsen, the **heat of formation** of the hexahydrate in aq. soln. is $(Ni,O,N_2O_5,Aq.)=83·37$ Cals; $(Ni,\frac{1}{2}O_2,2HNO_3,Aq.)=83·42$ Cals.; $(Ni,N_2,3O_2,6H_2O)=120·71$ Cals. The **heat of neutralization,** $\frac{1}{2}Ni(OH)_2$, by HNO_3aq. is 10·546 Cals. A. Guntz and F. Martin gave 11·88 Cals. for the **heat of solution** of the anhydrous nitrate in 200 mols. of water at 18°; and for a mol. of the hexahydrate in 400 mols. of water, J. Thomsen gave −7·47. J. Thomsen also found for $Ni(NO_3)_2Aq.+H_2S=NiS+2NHO_3aq.$ −4·9 Cals.

W. V. Bhagwat, J. Angerstein, and H. Emsmann measured the **absorption spectra** of soln. of nickel nitrate—*vide supra.* H. M. Vernon studied the changes in **colour** which occur on diluting, and on raising the temp. of aq. soln. E. J. Houston observed that the pale green, aq. soln. becomes greenish-yellow when heated. H. C. Jones and F. H. Getman found the **indices of refraction** of aq. soln., μ, with M mols. of the nitrate per litre, to be:

M .	0·0761	1·1522	0·3044	0·6088	0·7610	1·0654	1·2176	1·5220
μ . .	1·32782	1·32989	1·33378	1·34277	1·34667	1·35463	1·35870	1·36653

F. Allison and E. J. Murphy studied the **magneto-optical properties** of the salt.

The **electrical conductivity** of soln. with $\frac{1}{2}Ni(NO_3)_2$ in v litres at 25°, were found by E. Franke to be:

v	32	64	128	256	512	1024
λ	94·48	99·86	103·9	108·6	110·8	113·3

and A. Rosenheim and V. J. Meyer gave for soln. with a mol of the salt in v litres of water, or alcohol, at 25°:

v	64	128	256	512	1024
μ Water .	213	226	234	241	246
μ Alcohol .	19·5	22·5	26·2	29·1	31·5

H. C. Jones and J. N. Pearce measured the mol. conductivity, μ, and calculated the corresponding percentage **ionization,** a :

v .	0·5	1·0	2·0	10	20	40	100
μ .	35·61	57·38	71·44	87·84	93·57	100·31	106·77
a .	30·38	48·95	60·95	74·94	79·83	85·58	91·10

The subject was discussed by S. Jakubsohn and M. Rabinowitsch, W. H. Banks and co-workers, and A. Heydweiller. E. Rona studied the **mobility of the ions ;** A. A. Groening and H. P. Cady, the decomposition potential. H. C. Jones and co-workers calculated the **solvation** of soln. with C mols per litre from the conductivity and f.p. data. Let the degree of solvation be represented by the number of mols. of water in combination with a mol. of salt if a litre of the soln. at that concentration contained 1000 grms. of water.

C . .	0·0761	0·3044	0·7610	1·2176	1·5220	2·0000	2·5000
Solvation .	28·1	25·4	21·1	20·1	18·8	17·4	15·6

A. Klemenc and H. F. Hohn studied the electrolysis; and E. Bouty, the **thermoelectric force** of aq. soln. O. Liebknecht and A. P. Wills gave 24×10^{-6} mass unit for the **magnetic susceptibility** of soln. of the nitrate at 18° ; and G. Jäger and S. Meyer, 25×10^{-6} mass unit. P. Philipp, L. A. Welo, A. Duperior, R. B. James, and B. Cabrera and co-workers studied the subject.

According to W. Ipatéeff and B. Muromtzeff, with **hydrogen** under a press. of 50 to 250 atm., and at about 200°, a soln. of nickel nitrate, in gold tubes, furnishes $Ni(NO_3)_2.4NiO.2H_2O$, mixed with some nickel oxide if the temp. rises to 270° ; in quartz tubes, between 200° and 240°, $Ni(NO_3)_2.5NiO$, is deposited ; at 245°, $Ni(NO_3)_2.3NiO$, is formed ; and between 330° and 360°, nickel oxide is produced. J. H. Weibel studied the reaction ; and S. Miyamoto, the reduction by hydrogen in the silent discharge. J. C. G. de Marignac observed that crystals of the nitrate do not deliquesce in **air** in dry weather, and R. Tupputi showed that the crystals of the hexahydrate effloresce slightly or deliquesce rapidly in air according to the degree of humidity of the atmosphere. The subject was studied by W. Rückert, and M. A. Rakuzin. A. Mailfert observed that the hexahydrate is slowly attacked by **ozone.** The solubility of the salt in **water** has been discussed. Our knowledge of the nature of the basic salts is unsatisfactory. J. L. Proust noted that when the hydrate is heated at a low temp., it forms a basic salt, and J. Habermann obtained a precipitate of **nickel oxynitrate,** $8NiO.2N_2O_5.5H_2O$, by adding a soln. of the normal salt to insufficient alkali lye to precipitate all the nickel. G. Rousseau and G. Tite heated hydrated nickel nitrate with fragments of quicklime in a sealed tube at 350°, and obtained green crystals of $5NiO.N_2O_5.4H_2O$, which are not decomposed by boiling water. W. Feitknecht found that the lattice of $Ni(NO_3)_2.4Ni(OH)_2$ corresponded with alternate layers of normal salt and hydroxide. R. Schwarz observed that **nickel amminochloronitrate,** $6Ni(NO_3)_2.NiCl_2.30NH_3.16H_2O$, can be prepared by the action of ammonia on a soln. of the component salts. The azure-blue, octahedral crystals are soluble in water, but the aq. soln. decomposes with the separation of nickel hydroxide and the liberation of ammonia. A. Guntz, F. Friedrichs, R. Taft and H. Barham, and E. C. Franklin and C. A. Kraus observed that the hexahydrate is soluble in liquid **ammonia.** The subject was studied by F. Friedrichs. H. Hunt and L. Boncyk said that it is insoluble in liquid ammonia at 25°. A. Guntz and F. Martin prepared pale violet crystals of **nickel enneamminonitrate,** $Ni(NO_3)_2.9NH_3$, by the action of finely-divided nickel on a soln. of silver nitrate in liquid ammonia. The compound loses ammonia when heated slowly, or in vacuo, but before all the ammonia is evolved, some nitrous fumes are formed. The salt is decomposed by water, precipitating nickel hydroxide. H. J. S. King and co-workers prepared **nickel hexamminonitrate,** $[Ni(NH_3)_6](NO_3)_2$, and measured the depression of the f.p. in soln. O. L. Erdmann, and A. Laurent obtained **nickel diaquotetramminonitrate,** $[Ni(NH_3)_4(H_2O)_2](NO_3)_2$, by strongly cooling, or by adding alcohol to a conc. soln. of nickel nitrate in aq. ammonia.

O. L. Erdmann added that the sapphire-blue, transparent, regular octahedra give off ammonia when exposed to air, and slowly crumble to a bluish-white powder which deliquesces in moist air. The salt fuses when heated, first giving off water and ammonia, and afterwards nitrous vapours with a slight detonation, leaving behind a residue of nickelous oxide. When heated in air, or on a platinum foil, the salt burns with a vigorous detonation leaving behind black nickelous oxide mixed with a little peroxide. The salt is freely soluble in cold water, and somewhat soluble in dil alcohol. The blue aq. soln. gives off ammonia when boiled, and flakes of hydrated nickelous oxide, and ammonium nitrate are formed in the liquid. The dil. soln. decomposes quickly even as it begins to boil, but the conc. soln. remains blue even when boiled. G. André failed to prepare the diaquotetrammine, but obtained the hydrated hexammine, $2[Ni(NH_3)_6](NO_3)_2.3H_2O$, by passing ammonia into a soln. of nickel nitrate, or into a soln. of ammonium nitrate holding nickel oxide in suspension. R. W. G. Wyckoff considered that some mistake has been made in assuming that the diaquotetrammine is formed because he always obtained the hexamminonitrate, $Ni(NO_3)_2.6NH_3$, in blue, isotropic octahedra, by adding an excess of conc. aq. ammonia to an aq. soln. of nickel nitrate. F. Ephraim obtained the hexammine by the action of dry ammonia on the anhydrous nitrate. E. Kocsis, and F. C. Kracek and co-workers studied the structure of the hexammine. R. W. G. Wyckoff found that the X-radiograms of the crystals correspond with a lattice resembling that of the hexamminohalides with 4 atoms of nickel for each elementary cell, and having the NH_3-groups similarly oriented, but with the halogen groups replaced by NO_3-groups. The side of the unit, cubic cell is $a=10{\cdot}96$ A. F. Ephraim and P. Mosimann, and P. Mosimann found the solubility in water to be 44·55 grms. or 0·156 mol. per litre.

T. W. B. Welsh and H. J. Broderson found that 100 c.c. of anhydrous **hydrazine** dissolve 3 grms. of anhydrous nickel nitrate at room temp.; and, according to H. Franzen and O. von Meyer, **nickelous trihydrazinonitrate,** $Ni(NO_3)_2.3N_2H_4$, is formed when 12 grms. of the diaquotetramminonitrate are treated with 20 c.c. of 50 per cent. hydrazine hydrate and the mixture warmed on a water-bath. The crystals are washed successively with water, alcohol, and ether, and dried in vacuo over sulphuric acid, and potassium hydroxide. The salt also formed as a reddish-violet precipitate on adding 10 c.c. of hydrazine to a soln. of 10 grms. of nickel nitrate in 100 c.c. of warm water, and allowing the mixture to stand on a water-bath. The blue soln. becomes nearly colourless as the crystals are deposited. The reddish-violet powder is insoluble in water; and it is decomposed by hot water; it is soluble in dil. acids; it explodes vigorously when heated in a porcelain crucible. A. Ditte observed that nickel nitrate is but sparingly soluble in **nitric acid.**

J. H. Weibel studied the action of **carbon monoxide.** R. Tupputi said that the hexahydrate is soluble in **alcohol.** F. W. O. de Coninck showed that **glycol** dissolves 7·5 per cent. $Ni(NO_3)_2$ at room temp. A. Naumann found that the nitrate is insoluble in **benzonitrile**; K. P. McElroy and W. H. Krug, that the hexahydrate is slightly soluble in **acetone**; and A. Naumann, that it is insoluble in **ethyl acetate,** and very sparingly soluble in **methyl acetate.** A. V. Dumansky and B. G. Zaprometoff studied the complexes with **tartrates,** and with **mannitol.** J. Dalietos, and H. Werner and W. Spruck observed that with **ethylenediamine,** there is formed **nickel trisethylenediaminonitrate,** $[Ni\ en_3](NO_3)_2$, in dark violet plates whose absorption spectrum was studied by J. Angerstein; A. Rosenheim and V. J. Meyer, that with **thiocarbamide** it forms **nickelous thiocarbamidonitrate,** $Ni(CSN_2H_4)(NO_3)_2$, in greenish-yellow prisms; J. Moitessier, that with **phenylhydrazine** it forms **nickel tetraphenylhydrazine,** $Ni(NO_3)_2.4C_6H_5N_2H_4$, in pale blue, microscopic, rhomboidal plates; J. Frejka and L. Zahlova prepared **nickel trisbutylenediaminonitrate,** $[Ni\ bn_3](NO_3)_2.H_2O$, in red crystals; M. Papafil, and R. Cernatescu and co-workers, **phenylenediamines**; and M. Poni, compounds with cyclic amines—$C_6H_3(CH_3)(NH_2)_2$, and $C_{10}H_6(NH_2)_2$. G. T. Morgan and

F. H. Burstall observed that with **αα′-dipyridyl,** nickel nitrate forms **nickel tris-αα′-dipyridylnitrate,** $[Ni(C_{10}H_8N_2)_3](NO_3)_2.6H_2O$; and H. J. S. King and co-workers prepared **nickel hexapyridinonitrate,** $[Ni(C_5H_5N)_6](NO_3)_2$, and measured the depression of the f.p. of the salt. W. Hieber and E. Levy studied the complex with **monoethylolamine ;** K. A. Jensen and E. Rancke-Madson, one with **thiosemicarbazide ;** A. Tettamanzi and B. Carli, one with **triethanolamine ;** K. A. Jensen, **nickel xanthogenonitrate.** J. E. Heck and M. G. Mellon observed the rhythmic precipitation from soln. of the nitrate in silica and agar-agar gels containing dicyandiamidine sulphate, phenylthiohydantoic acid, and dimethylgloxime. I. W. Schmoss observed that yellow **phosphorus** in an atm. of carbon dioxide, when boiled with an alcoholic soln. of nickel nitrate forms pale green nickel phosphate. According to S. Papiermeister, a soln. of nickel nitrate yields a complex salt when treated with **mercuric cyanide,** namely, $Ni(NO_3)_2.2HgCy_2.6\frac{1}{2}H_2O$. T. Heymann and K. Jellinek studied the reaction with **cobalt :** $Ni^{\cdot\cdot}+Co \rightleftharpoons Ni+Co^{\cdot\cdot}$.

A. Mailhe reported **copper nickel trioxynitrate,** $Ni(NO_3)_2.3CuO.3H_2O$, or, according to A. Werner, $Cu_2(OH)_4Cu : (OH)_2.Ni(NO_3)_2$, to be formed by boiling hydrated copper oxide with a soln. of nickel nitrate. The green, hexagonal prisms are isomorphous with the corresponding zinc salt. W. A. Endriss studied this salt. T. Koepplowna studied the solid soln. of **nickel-zinc nitrates.** A number of double nitrates with the rare earth salts have been formed by mixing soln. of the component salts. F. T. Frerichs and E. F. Smith reported **lanthanum nickel nitrate,** $2La(NO_3)_3.3Ni(NO_3)_2.36H_2O$, and G. Jantsch prepared $Ni_3[La(NO_3)_6]_2.24H_2O$, in pale green, hexagonal crystals, of sp. gr. 2·146 at 0°/4°, and m.p. 110·5° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 8·03 grms. of the hydrated salt at 16°. G. Jantsch prepared **cerous nickel nitrate,** $Ni_3[Ce(NO_3)_6]_2.24H_2O$, in dark green crystals of sp. gr. 2·173 at 0°/4°, and m.p. 108·5° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 7·53 grms. of the hydrated salt at 16°. R. J. Meyer and R. Jacoby, M. Holzmann, and H. Zschiesche prepared **ceric nickel nitrate,** $Ni[Ce(NO_3)_6].8H_2O$, in brown crystals from a soln. of the component salts in nitric acid. R. J. Meyer and R. Jacoby obtained **thorium nickel nitrate,** $Ni(Th(NO_3)_6].8H_2O$, in pale green crystals. F. T. Frerichs and E. F. Smith reported a *didymium* nickel nitrate, $2Di(NO_3)_3.3Ni(NO_3)_2.36H_2O$. G. Jantsch prepared **praseodymium nickel nitrate,** $Ni_3[Pr(NO_3)_6]_2.24H_2O$, in dark green crystals, of sp. gr. 2·195 at 0°/4°, and m.p. 108° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 9·28 grms. of the hydrated salt at 16°. G. Jantsch obtained **neodymium nickel nitrate,** $Ni_3[Nd(NO_3)_6].24H_2O$, in bluish-green crystals of sp. gr. 2·202 at 0°/4°, and m.p. 105·6° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 11·66 grms. of the hydrated salt at 16°. G. Jantsch prepared **samarium nickel nitrate,** $Ni_3[Sm(NO_3)_6]_2.24H_2O$, in green crystals of sp. gr. 2·272 at 0°/4°, and m.p. 92·2° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 29·11 grms. of the hydrated salt. G. Urbain prepared **gadolinium nickel nitrate,** $2Gd(NO_3)_3.2Ni(NO_3)_2.24H_2O$, or, according to G. Jantsch, $Ni_3[Gd(NO_3)_6]_2.24H_2O$, in green crystals of sp. gr. 2·356 at 0°/4°, and m.p. 72·5° ; 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 40·08 grms. of the hydrated salt at 16°. G. Urbain and H. Lacombe obtained **bismuth nickel nitrate,** $Ni_3[Bi(NO_3)_6]_2.24H_2O$, in green crystals of sp. gr. 2·51 at 16°/16°, and m.p. without decomposition at 69°. G. Jantsch added that 100 c.c. of a sat. soln. in nitric acid of sp. gr. 1·325 contain 46·20 grms. of the hydrated salt at 16°. A. Lancien obtained **uranyl nickel**

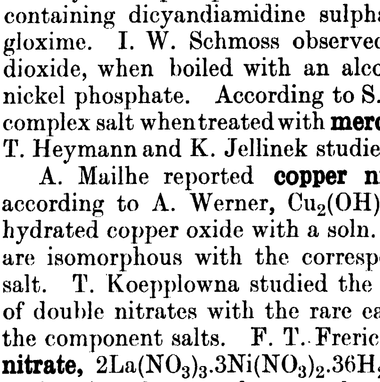

FIG. 371.—Equilibrium Diagram of the Nickel-Cobalt Nitrates.

nitrate, $2UO_2(NO_3)_2.10Ni(NO_3)_2$, in greenish-yellow crystals. T. Koepplowna studied the solid soln. of **manganese-nickel nitrates.** A. Benrath and W. Thiemann studied the **cobalt-nickel nitrates.** The results, summarized in Fig. 371, show solid soln. of the two salts, and the conditions of equilibrium of the hydrates.

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§ 21. Nickel Phosphates

R. Tupputi[1] observed that **nickel orthophosphate**—according to the analyses of C. F. Rammelsberg, $Ni_3(PO_4)_2.8H_2O$—is precipitated in the form of apple-green plates or emerald-green crystalline granules, when a soln. of a nickel salt is treated with sodium hydrophosphate. W. Skey could not obtain the crystalline salt. The earlier workers regarded it as the heptahydrate, but F. Ephraim and C. Rossetti showed that it is octohydrated. H. Bassett and W. L. Bedwell prepared this salt. N. S. Kurnakoff and I. A. Andreevsky found arrests at 110°, 220°, and 260° on the dehydration curve. C. F. Rammelsberg found that the salt after calcination is slightly sintered, and yellow; H. Struve observed that the dehydrated salt does not lose weight at a red-heat, but it is browned by the operation; since the residue has the composition $5NiO.2P_2O_5$, he inferred that the salt has the composition $Ni_3(PO_4)_2.2NiHPO_4$. He also found that at a white-heat, the phosphate is reduced to phosphide, and H. Rose showed that this also is the case when the phosphate is heated in hydrogen. R. A. Fereday studied the magnetic susceptibility. According to C. F. Rammelsberg, the orthophosphate is insoluble in water, and freely soluble in acids. F. Ephraim and A. Schärer prepared complexes with halide acids—*e.g.*, $Ni_3(PO_4)_2.2H_2O.6HCl$, and $(Ni_3(PO_4)_2.2H_2O.7HBr$. H. Rose found that the phosphate is soluble in a soln. of a nickel salt; R. Tupputi, that it is insoluble in a soln. of sodium hydrophosphate, and slightly soluble in a hot soln. of ammonium hydrophosphate; and A. Naumann, that it is insoluble in methyl and ethyl acetates. R. Tupputi found that if a soln. of the orthophosphate in aq. ammonia be boiled until ammonia is no longer evolved, pale apple-green flecks containing nickel, phosphoric acid, and ammonia separate out. O. L. Erdmann noted that when alcohol is added to an ammoniacal soln. of nickel orthophosphate, a pale bluish-green precipitate containing ammonia separates out, and if a layer of alcohol is poured over the aq. soln., crystals of the ammine are formed. J. Persoz observed that if the ammoniacal soln. of nickel orthophosphate be exposed to air, the whole of the nickel separates as a grey precipitate which changes to a green colour. N. A. Yajnik and F. C. Trehana studied the action of the carbonate on the photochemical reduction of sugars. W. Muthmann and H. Heramhof tried nickel phosphate as a porcelain pigment.

H. Debray prepared **ammonium nickel orthophosphate,** $(NH_4)NiPO_4.2H_2O$, by heating to 80° a mixed soln. of nickel sulphate and an excess of ammonium phosphate, and digesting the precipitate with the mother-liquor for crystals of the *dihydrate.* G. Chancel obtained the *hexahydrate*, by adding ammonium phosphate to a soln. of a nickel salt, and digesting the precipitate with the precipitant in order to convert it into the crystalline state. The salt forms nickel pyrophosphate when calcined ; it is soluble in aq. ammonia, and in acids ; and H. Debray noted that boiling water decomposes it into nickel and ammonium phosphates. L. Ouvrard obtained **potassium nickel orthophosphate,** $KNiPO_4$, by fusing nickel oxide with potassium pyrophosphate, hydrophosphate, or orthophosphate ; or nickel orthophosphate and potassium chloride. The rhombic crystals are soluble in acids. L. Ouvrard also obtained monoclinic crystals of $2K_3PO_4.Ni_3(PO_4)_2$, by melting potassium metaphosphate with nickel oxide. H. Grandeau also obtained potassium nickel phosphates by fusing nickel orthophosphate with potassium sulphate. H. Bassett and W. L. Bedwell prepared the hydrates $KNiPO_4.6H_2O$, and $KNiPO_4.H_2O$. J. J. Berzelius heated nickel oxide with microcosmic salt in the blowpipe flame and observed that the blue coloration disappears as the glass cools. L. Ouvrard obtained rhombic prisms of **sodium nickel orthophosphate,** $NaNiPO_4$, by fusing sodium metaphosphate with an excess of nickel oxide in the presence of sodium chloride. If the nickel oxide be not in excess, crystals of $Na_3PO_4.NaNiPO_4$, isomorphous with the corresponding zinc salt, are produced. H. Debray reported crystals of the *heptahydrate,* $NaNiPO_4.7H_2O$, to be formed by adding sodium hydrophosphate to a soln. of a nickel salt, and digesting the precipitate with the mother-liquor for some time. This salt was also investigated by H. Bassett and W. L. Bedwell.

W. Skey prepared **magnesium nickel orthophosphate,** by adding a soluble phosphate to a soln. of a salt of nickel in the presence of enough acid to keep the liquid acidic. The gelatinous precipitate becomes crystalline if it is allowed to stand for a few days in the mother-liquor. H. Rose also obtained it by adding an excess of ammonia to an acidic soln. of a nickel and magnesium salt, in the presence of phosphoric acid. W. Skey also prepared **zinc nickel orthophosphate** in a similar manner.

M. Stange,[2] P. Glühmann, and F. Schwarz observed that when soln. of a nickel salt and of sodium triphosphate are so diluted that no precipitation occurs when they are mixed, and the mixed soln. is evaporated, spontaneously, then green, rhombic crystals of **sodium nickel triphosphate,** $Na_3NiP_3O_{10}.12H_2O$, are formed isomorphous with the crystals of the corresponding cobalt salt. When heated, the salt turns yellow, and at a red-heat melts to form a brown glass. The salt is insoluble in water, and is not decomposed by the liquid. The salt, after having been fused, is readily soluble in acids.

A. Schwarzenberg [3] and C. F. Rammelsberg prepared **nickel pyrophosphate,** $Ni_4P_2O_7.nH_2O$, by adding sodium pyrophosphate to a soln. of a nickel salt, and G. Chancel, by calcining ammonium nickel orthophosphate. The pale green hydrated salt loses 26·05 per cent. of water when it is dried at 110°, and it becomes yellow on ignition. F. W. Clarke gave 3·9303 for the sp. gr. at 25°, and 3·9064 for the sp. gr. at 27°. A. Reynoso found that when the salt is heated with water to 280° or 300°, it forms an acid nickel phosphate which remains in soln., and heptahydrated nickel orthophosphate which is precipitated. According to A. Schwarzenberg, the salt is soluble in mineral acids, in an aq. soln. of sodium pyrophosphate, and in aq. ammonia ; if cobalt is also present, the addition of alcohol to the ammoniacal soln. precipitates the cobalt pyrophosphate before the nickel salt. If the precipitate is dissolved in sulphurous acid, the nickel salt is deposited from the soln. in the crystalline state ; and if cobalt is present, the cobalt salt is precipitated first. W. Daller studied the action of hydrazine; and G. Sartori, some electrolytic properties of the salt.

According to K. A. Wallroth, by adding nickel oxide to molten microcosmic

salt until saturated, and then cooling the product, yellow, prismatic crystals of **sodium nickel pyrophosphate,** $4Na_4P_2O_7.5Ni_2P_2O_7$, are formed which can be melted to a brown glass. The crystals are insoluble in water, but soluble in acids. L. Ferrand prepared **nickel thiophosphate,** $Ni_2P_2S_7$, as a deep brown crystalline powder.

According to G. Tammann,[4] a soln. of nickel sulphate causes sparingly soluble ammonium metaphosphate to swell up to form a transparent, resinous mass, which dissolves in an excess of the nickel sulphate soln. The addition of water to the soln. precipitates a resinous mass. If an eq. proportion of a soln. of nickel sulphate is allowed to act on lithium metaphosphate, part of the lithium is slowly displaced by the nickel. This is the nearest approach to **lithium nickel metaphosphate** so far obtained. R. Maddrell obtained **sodium nickel metaphosphate,** $NaPO_3.3Ni(PO_3)_2$, by evaporating a mixture of phosphoric acid, sodium hydroxide, and nickel sulphate to dryness, and then heating the residue to 316°. The green powder is insoluble in water and dil. acids, but soluble in conc. sulphuric acid.

R. Maddrell prepared **nickel dimetaphosphate,** $Ni(PO_3)_2$, by evaporating to dryness a mixture of nickel oxide and an excess of dil. phosphoric acid, and then heating the product to 316°. P. Hautefeuille and J. Margottet obtained it by heating nickel oxide with molten metaphosphoric acid. The greenish-yellow crystals are insoluble in water and in dil. acids, but soluble in conc. sulphuric acid, and, according to A. Glatzel, in boiling conc. nitric and hydrochloric acids. The salt melts at a red-heat, and crystallizes on cooling. When digested for a long time with a soln. of alkali sulphate, nickel sulphide and alkali metaphosphate are formed. A. Glatzel prepared the *tetrahydrate,* $Ni(PO_3)_2.4H_2O$, mixing conc. soln. of alkali dimetaphosphates and nickel chloride. The yellowish-green, acicular crystals lose all the water of hydration at 200°. The salt is not altered by a feeble calcination, but at a higher temp., the salt fuses, and on cooling furnishes crystals of the tetrametaphosphate. One part of the salt dissolves in 2·5 parts of cold water; it is freely soluble in acids in the cold, and when the acidic soln. is boiled, phosphoric acid is formed.

A. Glatzel prepared **ammonium nickel dimetaphosphate,** $(NH_4)_2Ni(P_2O_6)_2.4H_2O$, by mixing a soln. of ammonium dimetaphosphate with the corresponding proportion of nickel chloride, and allowing the mixture to stand for some time, when bluish-green crystals of the tetrahydrate are formed. The salt loses water at 150°, and becomes dark green, but no other change is perceptible; at a higher temp., ammonia is given off. The last traces of ammonia are retained somewhat tenaciously. When the salt is fused and then cooled, it yields a glass. One part of the salt dissolves in 12·5 parts of cold water; the salt also dissolves in acids with the liberation of phosphoric acid. A. Glatzel obtained **potassium nickel dimetaphosphate,** $K_2Ni(P_2O_6)_2.6H_2O$, by mixing soln. of eq. proportions of potassium dimetaphosphate and nickel chloride. The pale green crystals lose their water of crystallization when feebly calcined without suffering any other change; and when strongly heated, the salt fuses, and then solidifies to a clear glass. The salt is very sparingly soluble in water; 100 parts of water dissolve 0·77 part of the salt; the glassy salt is completely soluble in acids; an alkali sulphide has very little action on the salt. The crystals are easily decomposed by acids, and the boiling acid produces orthophosphoric acid; molten sodium carbonate decomposes the salt. A. Glatzel prepared **sodium nickel dimetaphosphate,** $Na_2Ni(P_2O_6)_2.6H_2O$, by an analogous process. The water of hydration is expelled by a feeble calcination; is very sparingly soluble in water; it is easily soluble in acids; and melts at a red-heat.

G. Tammann treated sodium metaphosphate with nickel chloride or sulphate, and obtained **sodium nickel trimetaphosphate,** $Na_2Ni_2(P_3O_9)_2.9H_2O$. It melts at a dull red-heat; and 1 part of the salt dissolves in 66·6 parts of water at 20°. C. G. Lindbom also prepared $Na_4Ni(P_3O_9)_2.8H_2O$.

A. Glatzel prepared **nickel tetrametaphosphate,** $Ni_2P_4O_{12}$, by fusing and then

cooling the dimetaphosphate. Dirty green crystals are obtained, when purified the colour is yellow. The salt is insoluble in hydrochloric acid, but soluble in conc. nitric and sulphuric acids when boiled. When fused with sodium carbonate, the ordinary metaphosphate is formed. When treated with sodium sulphide, it is converted into nickel sulphide and alkali tetrametaphosphate, slowly in the cold, rapidly at 50°. The *dodecahydrate*, $Ni_2P_4O_{12}.12H_2O$, is obtained by mixing conc. soln. of alkali tetrametaphosphate and nickel chloride. The green crystals lose half their water of hydration at 100°, and the remaining 6 mols. at 150°. When melted and cooled it forms a dirty green-coloured glass. One part of the salt requires 22 parts of water for soln. The hydrate is rapidly decomposed by boiling acids, but the calcined salt is decomposed slowly.

H. Rose found that a soln. of nickel chloride gives a precipitate, presumably **nickel hexametaphosphate,** $Ni_3P_6P_{18}.nH_2O$, when it is treated with sodium hexametaphosphate, but not so with a soln. of nickel sulphate. The pale green, gelatinous mass is soluble in an excess of the precipitant. According to H. Lüdert, when the fused product is cooled, it forms a clear glass, and the powdered glass is insoluble in water, but the gelatinous salt is sparingly soluble in water, and is precipitated from the soln. on the addition of alcohol.

G. Tammann melted ammonium sodium phosphate with nickel sulphate, and obtained **sodium nickel octometaphosphate,** $Na_2Ni_3P_8O_{24}$, as a deep yellow powder consisting of crystals which are combinations of cubes and octahedra.

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CHAPTER LXIX

RUTHENIUM

§ 1. The Occurrence of Ruthenium

THE history of ruthenium is discussed in connection with the platinum metals. Ruthenium was found by F. Wöhler [1] to occur as the mineral *laurite*, RuS_2, or $(Ru,Os)S_2$, in the platinum washings of the Transvaal, Borneo, and Oregon. H. St. C. Deville and H. Debray, and C. Claus, observed that the ruthenium favours the osmiridium, and they observed 6·37 per cent. in that mineral from Columbia ; 0·50 per cent. in a sample from California ; 5·22 per cent. in one from Australia ; and 0·20 to 8·49 per cent. in samples from the Urals. C. Langer and C. Johnson found 0·39 per cent. of Ir, Rh, and Ru, in the residues after extracting nickel and copper from the Sudbury nickel-copper sulphide ores. There were also present 1·85 per cent. Pt ; 1·91, Pd ; 0·56, Au ; and 15·42, Ag. When ruthenium is required, it is usually extracted from osmiridium. Ruthenium-syserskite has 18·3 per cent. of ruthenium ; and ruthenium-neujanskite, 4·7 to 13·4 per cent. S. Iimori and J. Yoshimura said that a pink china clay from Tanokami, Japan, contained rhodium or ruthenium as a minor constituent.

The general occurrence of ruthenium is discussed in connection with the platinum metals. F. W. Clarke and H. S. Washington's [2] estimate for the proportion of ruthenium in the igneous rocks of the earth's crust is of the order $n\times10^{-11}$; and I. and W. Noddack gave $2{\cdot}3\times10^{-8}$ for the earth's crust ; $2{\cdot}39\times10^{-5}$ for meteoric iron ; $4{\cdot}20\times10^{-6}$ for troilite ; and for the atomic distribution, oxygen unity, they gave $6{\cdot}1\times10^{-6}$; later, they gave $1{\cdot}8\times10^{-8}$ for the earth's crust, and 9×10^{-6} for meteorites. The distribution in the earth's crust, etc., was discussed by P. Niggli, V. M. Goldschmidt and C. Peters, F. Bernauer, and P. Vinassa. G. P. Merrill reported the presence of ruthenium in meteorites. M. N. Saha, and H. A. Rowland classed ruthenium amongst the elements whose presence in the sun is doubtful. According to H. von Klüber, twenty-four lines of the solar spectrum have been identified with those of ruthenium. The subject was discussed by H. N. Russell.

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§ 2. The Extraction and Preparation of Ruthenium

Osmiridium is an alloy of osmium and iridium containing small proportions of rhodium and ruthenium. In some cases, about 6 per cent. of ruthenium is present. E. Frémy,[1] and H. St. C. Deville and H. Debray found that when osmiridium is roasted in air or oxygen, much of the ruthenium is volatilized as oxide which can be easily reduced to the metal by heating it in a current of hydrogen. J. Persoz, O. W. Gibbs, and F. Weiss and F. Döbereiner fused the ore with a mixture of sulphur and sodium carbonate at a high temp.; C. Claus, with about ten times its weight of a mixture of potassium hydroxide and nitrate in the approximate proportions 4 : 1 to 1 : 4; A. Joly and H. Debray used the same mixture in the approximate proportions 4 : 1; A. Gutbier and C. Trenkner, F. Krauss and H. Kükenthal, and A. Guyard, 1 : 1. W. H. Wollaston, E. Frémy, and O. W. Gibbs also used potassium nitrate for opening up the ore. C. Claus, J. Fritzsche and H. Struve, and U. Antony and A. Lucchesi fused the ore with a mixture of equal parts of potassium hydroxide and chlorate; and O. Ruff and F. Vidic, a mixture of potassium hydroxide with one-tenth its weight of the permanganate. J. L. Howe, E. Leidié and L. Quennessen, and E. Wichers and coworkers used sodium dioxide with one-third or one-fourth its vol. of ore. F. Wöhler heated the ore mixed with sodium chloride at dull redness in a current of chlorine. The opening up of the platinum ores is discussed in connection with platinum. C. Claus obtained ruthenium from osmiridium, by washing the powdered mineral with hydrochloric acid, and then heating to low redness a mixture of it and sodium chloride in a current of moist chlorine. The aq. extract of the cold mass was concentrated, mixed with a few drops of ammonia and heated, whereupon osmic and ruthenic oxides were precipitated. Only part of the osmiridium is decomposed by the treatment with chlorine gas; and the treatment must be repeated on the undissolved residue three or four times in order to obtain complete decomposition. The precipitate of ruthenic and osmic oxides was washed with nitric acid, and heated with acid in a retort until the free acid and osmic acid had distilled over. The dry contents of the retort were fused with potassium hydroxide, and the cold mass dissolved in cold water. The clear liquid, separated from the sediment, was neutralized with nitric acid, when black ruthenic oxide was precipitated. The washed and dried oxide, when reduced in hydrogen, furnished powdered ruthenium.

In his first experiments, C. Claus obtained ruthenium from platinum residues by fusing the mixture with potassium nitrate, and extracting with water when potassium osmate, ruthenate, iridate, etc., passed into soln., but most of the ruthenium remained with the undissolved residue. This residue was mixed with about half its weight of aqua regia in a retort, and the liquid distilled nearly to dryness. Osmic acid collected in the receiver. The contents of the retort were mixed with water and filtered. The insoluble residue, A, was mixed with another residue obtained later. Potassium carbonate was added to the filtrate to precipitate ferric and ruthenic oxides. These oxides were dissolved in hydrochloric acid, and zinc added when some of the ruthenium is precipitated; the brown liquid, obtained as a filtrate from the ferric and ruthenic oxides, became colourless when allowed to stand in wooden vats, and when evaporated in iron vessels, the blue oxide of iridium separated out. This was dissolved in aqua regia, the iridium precipitated by the addition of potassium chloride, and the mother-liquor evaporated to dryness. The dry residue was reduced in hydrogen, and together with the product A, insoluble in aqua regia, was fused with its own weight of potassium nitrate for 2 hrs. at a white-heat. The cold mass, when extracted with water, gives a yellow soln. which, when treated with nitric acid, gives a black precipitate of impure potassium ruthenate. The hydrochloric acid soln. of this product was evaporated to dryness, and the aq. extract filtered to remove silica. The filtrate was treated with potassium chloride; the washed precipitate was reduced in hydrogen; and the product washed in water. There remained ruthenium as a dark grey powder.

H. St. C. Deville and H. Debray obtained ruthenium from osmiridium in the following manner:

The mineral was heated with four to five times its weight of zinc in a carbon crucible, at a white-heat, until the vapour of zinc ceased to be evolved. The friable mass was

crushed and heated with a mixture of barium dioxide and nitrate in a fireclay crucible at about 900°. The cold mass was treated with dil. hydrochloric acid whilst being cooled by immersion in cold water. The toxic fumes of osmic acid which may be evolved renders it advisable to conduct the operation in a fume chamber. Nitric and sulphuric acid were added to the cold liquid to precipitate barium sulphate; and the clear liquor was distilled until about one-fourth of its vol. had been collected in the receiver. This liquor was worked up for osmium (*q.v.*). The residue was evaporated to a smaller vol., treated with ammonium chloride and nitric acid, and evaporated to dryness on a water-bath. The bluish-black residue was washed with water half saturated with ammonium chloride until the washings were colourless. The residual ammonium chloroiridate, containing ruthenium, was ignited for the spongy metal which was then fused with potassium hydroxide and nitrate, in a silver crucible, and the cold mass dissolved in water. The addition of nitric acid to the yellow soln. precipitated ruthenium oxide. This was mixed with a little chalk and ignited in a graphite crucible. The chalk was afterwards removed by dil. acid. It was employed in order to remove any silica, chromium or osmium oxides which might be present. The metal can be purified by one or more fusions with the potassium hydroxide and nitrate mixture.

O. W. Gibbs recommended removing iridium and rhodium from soln. with other platinum metals by treatment with cobaltic luteochloride which precipitates cobaltic hexamminochloroiridate and hexamminochlororhodate. He also recommended the following process:

The potassium chlororuthenate is heated with a soln. of potassium nitrite to convert the ruthenium into the soluble, yellow potassium nitritoruthenate whilst the soln. is kept neutral or alkaline with potassium carbonate. The soln. is evaporated to dryness in a water-bath; and the cold product powdered and boiled with absolute alcohol in a flask fitted with a reflux condenser, until all is dissolved. The soln. is filtered, and the insoluble residue washed with absolute alcohol until the runnings give no precipitate with ammonium sulphide. The alcohol is distilled off, and the residue in the retort evaporated with hydrochloric acid to decompose the complex nitrite. Most of the platinum remains with the salt insoluble in alcohol. The soln. is evaporated with an excess of a sat. soln. of ammonium chloride, redissolved, and again evaporated. The dry mass is washed with a little cold water to remove alkali chlorides. The ammonium chlororuthenate is dissolved in hot water, ammonia is added, and the liquid is boiled and evaporated to dryness. The resulting yellow ruthenium diamminochloride is dissolved in water and treated with a soln. of mercuric chloride. The complex salt of ruthenium mercuric diamminochloride is soluble in boiling water and almost insoluble in cold water. It is therefore recrystallized from soln. in boiling water. This salt, on ignition, yields ruthenium as a silver-white porous mass.

The product obtained by the process of H. St. C. Deville and H. Debray still contains small quantities of osmium and iridium. A. Gutbier and C. Trenkner, and K. Trenkner heated the powder at a dull red-heat in a current of oxygen for about 3 hrs. in order completely to volatilize the osmium as tetroxide; the ruthenium is at the same time partially oxidized, and it is reduced by heating it in a current of hydrogen for about an hour. The product is fused in a silver vessel along with its own weight of potassium nitrate, and 8·3 times its weight of potassium hydroxide. The cold cake is extracted with water, and a rapid stream of chlorine is passed through the cold soln., and later the temp. is raised from 80° to 90°. The volatile ruthenium tetroxide is collected in an aq. soln. of potassium hydroxide cooled by a freezing mixture of ice and salt. No other metal present yields a volatile product under these conditions. On adding absolute alcohol to the distillate, a black precipitate is obtained. If the ruthenium tetroxide be not all dissolved in the alkali lye, J. L. Howe observed that alcohol may start an explosive reaction. Finally, the black precipitate of partially reduced ruthenium is completely reduced by heating it in a current of hydrogen. *Vide* Bunsen's process for rhodium. K. Hessner discussed the discovery of ruthenium.

Ruthenium and osmium form volatile tetroxides which can be distilled from a soln. at or near its b.p. Both metals form tetroxides when alkaline soln. of these metals are sat. with chlorine. Osmium alone is distilled off in the presence of nitric acid. Ruthenium chloride forms a soluble alkali ruthenate when treated with soda lye. J. L. Howe and F. N. Mercer brought the metal into soln. by the action of a conc. soln. of sodium hypochlorite containing some hydroxide. According to E. Wichers and co-workers, ruthenium can be readily converted into a

soluble ruthenate by fusion with 3 parts of sodium hydroxide and 1 part of sodium dioxide at 600° to 700° in a silver crucible—but a nickel or iron crucible can be used if there is no objection to introducing considerable amounts of these metals. Leaching such a melt with water extracts most of the ruthenium as soluble sodium ruthenate, Na_2RuO_4. Some of the ruthenium, however, may remain in the residue, especially if other metals, such as iridium, are present. This residue may be dried and fused again in order to complete the soln. of ruthenium, or extracted with a soln. of sodium hypochlorite. They recommended the following procedure for extracting or purifying the ruthenium—present in alkaline soln. as just indicated.

In the process of E. Wichers and co-workers the alkaline soln. containing ruthenium, associated with osmium (*q.v.*), is acidified with nitric acid, and 5 to 10 per cent. by vol. in excess is added. The soln. is distilled and the osmium tetroxide collected in a receiver. When the distillation of osmium tetroxide is completed, the cold soln. is made alkaline with sodium hydroxide, and an excess of 20 to 30 grms. per litre is added. The cold soln. is saturated with chlorine, after which the temp. is raised to 80° or 90° and the current of chlorine continued, but considerably diluted with air. At this temp. ruthenium tetroxide will distil quite rapidly. The receiving flasks contain hydrochloric acid diluted with 4 vols. of water and 1 vol. of alcohol, except that no alcohol should be added to the first flask. Care should be taken that the delivery tube and the first receiver are not cooler than about 25° to 30° to prevent stopping up the delivery tube with crystals of ruthenium tetroxide. When the oily droplets of ruthenium tetroxide no longer appear in the delivery tube, the soln. is boiled for a short time, continuing the current of chlorine mixed with air. After the distillation of ruthenium tetroxide seems to have stopped, more sodium hydroxide is added, and the current of chlorine continued, whereupon ruthenium tetroxide again distils. This operation is repeated as long as significant amounts of ruthenium tetroxide appear to distil. Small amounts of ruthenium and other metals remaining in the distilling flask may be recovered, as described in the section on general separations. The contents of the receiving flasks contain quadrivalent ruthenium chloride in the soln. containing no alcohol and mainly trivalent ruthenium chloride in the soln. containing alcohol. They are combined and evaporated to remove most of the excess of hydrochloric acid, after adding more alcohol if necessary. Some nitric acid is added to the residue and the soln. again evaporated to dryness. This should be repeated two or three times to remove any small amounts of osmium. If the original soln. has been distilled with nitric acid, the ruthenium soln. is not likely to contain enough osmium to warrant its recovery. The residue from the evaporation with nitric acid is evaporated once with hydrochloric acid. The residue is then taken up with water and distilled with chlorine from alkaline soln. as before. The second distillation eliminates small amounts of iridium or other impurities which may have been carried over mechanically in the first distillation. The ruthenium soln. in the receiving flasks are again evaporated with nitric acid, to remove any remaining traces of osmium. Finally, the residue is evaporated once with hydrochloric acid. It is now principally in the form of ruthenium nitrosochloride, $RuNOCl_3$, or the corresponding acid, $H_2RuNOCl_5$. This compound forms a relatively insoluble double salt with ammonium chloride similar to the salts of the other platinum metals. The precipitation of the double chloride converts the ruthenium to a form that may be ignited directly to sponge and also eliminates any small amounts of base-metal impurities. If a second precipitation is desired, the salt is decomposed with aqua regia and the resulting soln. evaporated to dryness. The residue is taken up in water, filtered from insoluble matter, and reprecipitated with ammonium chloride from a small vol. Because of the somewhat greater solubility of the ruthenium salt, it is better to use more concentrated soln. of ruthenium than can be used of the other platinum metals. The salt is filtered by suction, and washed with a 20 per cent. soln. of ammonium chloride or with alcohol.

The ruthenium left in the filtrates from the precipitation with ammonium

chloride can be recovered by evaporating to dryness, destroying the excess of ammonium chloride with nitric acid and finally igniting the entire residue in hydrogen. The removal of metals other than osmium during the process of purification may be followed by examining the metals left in the soln. in the distilling flask. The absence of significant amounts of osmium can be determined by distilling a portion of the ruthenium soln. with nitric acid and receiving the distillate in sodium hydroxide soln. containing a little alcohol. Even small amounts of osmium produce a violet-coloured soln.

According to R. Gilchrist and co-workers, osmium tetroxide alone is volatilized from soln. containing 40 per cent. of nitric acid by volume, and when distilled from alkaline hypochlorite soln., the ruthenium is incompletely eliminated; but if the ruthenium tetroxide is distilled from a soln. of sulphate in dil. sulphuric acid containing sodium bromate, a separation may be effected. The tetroxide is absorbed in hydrochloric acid (1 : 1), and a 10 per cent. soln. of sodium hydrocarbonate added until the acidity of the soln. reaches $p_H=6$ (bromocresol indicator). Boil, and filter for the hydrated oxide.

H. St. C. Deville and H. Debray obtained **crystalline ruthenium** by fusing the metal with an excess of tin in a carbon crucible, removing the excess of tin by boiling hydrochloric acid, and heating the unattacked residue, $RuSn_3$, in a current of hydrogen chloride to remove the tin as volatile chloride. There remain crystals of ruthenium. They also obtained dendrites and cubic crystals by heating the finely-divided metal with pyrites and borax. H. Moissan obtained crystals by distilling the metal in the arc-furnace. As indicated above, **spongy ruthenium** is formed by igniting ammonium chlororuthenate. According to E. Wichers and co-workers, in the fusion of crude osmium or osmiridium with sodium hydroxide and sodium dioxide, as described in the section on iridium, the soln. obtained by leaching the melt with water contains osmium as sodium osmate, Na_2OsO_4, and it also contains ruthenium and small amounts of the other platinum metals. Certain base metals, such as tin, lead, and zinc, may also be present. S. G. S. Dicker obtained **ruthenium films** by the thermal decomposition of a carbonyl. G. R. Levi and R. Haardt discussed the structure of the grains of **ruthenium black**; and A. A. Pollitt, its use as a catalytic agent.

E. Cohen and T. Strengers obtained **explosive ruthenium** by dissolving an alloy of zinc and ruthenium in hydrochloric acid; the zinc dissolves leaving the ruthenium as a finely-divided, explosive residue. Ruthenium is explosive even when the preparation is made in the absence of air, and in this respect it is unlike iridium and rhodium. With the two last-named metals, the explosiveness is attributed to the explosive combination of hydrogen and oxygen occluded in the metal; but with ruthenium the explosion occurs when no oxygen is present; hence the theory suggested by R. Bunsen, and H. Debray that the explosiveness may be due to the formation of an unstable, allotropic form of the metal which passes into the stable form with the evolution of much heat may be true.

A. Gutbier and co-workers prepared **colloidal ruthenium** by reducing a soln. of its salts by hydrazine hydrate in the presence of gum arabic as protective colloid; and by N. Castoro with acrolein as protective colloid. J. Donau found that a borax bead is coloured black by colloidal ruthenium.

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§ 3. The Physical Properties of Ruthenium

The reduced metal, in the form of a powder, is a dull grey **colour**, but A. Joly [1] found that the metal which has been fused in the arc furnace has a crystalline fracture, and it has a colour between that of iron and platinum. H. Moissan said that the **crystals** are pyramidal cubes. The **X-radiogram** of A. W. Hull corresponds with a close-packed, hexagonal lattice with the axial ratio $a:c=1:1\cdot59$; the side of the elementary, triangular prism is 2·686 A.; the distance between the nearest atoms in the basal plane is 2·686 A., and in the pyramidal planes, 2·640 A. The hexagonal lattice is said to be, like that of cadmium or zinc, composed of two, intermeshed lattices of right triangular prisms each with side $a=2\cdot686$ A., and height $c=4\cdot272$ A., and so arranged that the atoms of the one lattice are in the centre of the prisms of the other lattice. T. Barth and G. Lunde gave $a=2\cdot695$ A., $c=4\cdot293$ A.; E. A. Owen and co-workers, $a=2\cdot6987$ A., and $c=1\cdot5833$ A.; and $a:c=1\cdot586$; and G. R. Levi and R. Haardt, $a=2\cdot680$ A., $c=4\cdot261$ A., and $a:c=1:1\cdot59$. The subject was discussed by R. W. G. Wyckoff, and G. Natta. H. St. C. Deville and H. Debray gave 11·0 to 11·4 for the **specific gravity** of ruthenium; and later, 12·261 at 0. J. Violle gave 12·002; and A. Joly, 12·063 at 0°/4°, for the powdered metal. E. A. Owen and co-workers gave 12·45 calculated at 18°, and 12·2 observed. The value reported by C. Claus applied to a porous metal and is far too low. A. W. Hull calculated from the X-radiogram data, 12·56; and G. R. Levi and R. Haardt, 12·71. L. Pauling calculated 0·57 A. for the **atomic radius**; and V. M. Goldschmidt, 1·322 A. W. Biltz and K. Meisel, G. Hägg, J. C. Slater, E. H. Westling, W. H. Rothery, and P. Vinassa discussed the mol. vol. of ruthenium in its compounds. The **hardness** of the fused metal is comparable with that of iridium; and I. R. Rydberg found a hardness of 6·5 on Mohs' scale. It is 220 on Brinell's scale. A. Joly said that the metal is brittle when cold, but is somewhat malleable at a red-heat.

H. Fizeau found the coeff. of **thermal expansion** to be $\alpha=0\cdot0000091$ at 20°, and 0·00000963 at 40°, and that it increases by $0\cdot0_781$ per degree; S. Valentiner and J. Wallot found $\alpha=0\cdot0_5876$; and E. A. Owen and co-workers gave $9\cdot1\times10^{-6}$ for the mean coefficient of expansion. R. Bunsen found the **specific heat** between 0° and 100° to be 0·0611. H. Holzmann gave for the sp. ht., $c=0\cdot057439$

$+0{\cdot}0000189210\theta$. J. Dewar found that the sp. ht. in the temp. interval $-253°$ to $-196°$ is 0·0109. According to F. M. Jäger, and F. M. Jäger and E. Rosenbohm, the sp. ht. data indicate the existence of four enantiotropic or **allotropic forms.** There are **transition points** at 1035°, 1200°, and 1500°. The true sp. ht., C_p, of ruthenium is:

	0°	100°	200°	400°	600°	800°	1000°	1070°
C_p .	0·0551	0·0567	0·0583	0·0615	0·0648	0·0680	0·0712	0·664
	1100°	1200°	1300°	1400°	1450°	1500°	1550°	1600°
C_p .	0·0665	0·0730	0·0745	0·0745	0·0940	0·1075	0·0850	0·0566

The results for the corresponding atomic heats are plotted in Fig. 1. A. H. Stuart discussed the relation between the sp. ht. and the elastic constants. The sp. ht. of the α-form between 0° and 1000° can be represented by $C_p=0{\cdot}055066+0{\cdot}0_4161676\theta$. The sp. ht. between 1000° and 1070°, $C_p = 0{\cdot}070641 + 0{\cdot}0_357905(\theta - 1000) - 0{\cdot}0_575736(\theta-1000)^2$. The sp. ht. of the β-form, between 1070° and 1200°, is $C_p=0{\cdot}062078+0{\cdot}0_540379\theta$; that of the γ-form, between 1200° and 1400°, is $C_p=0{\cdot}055949+0{\cdot}0_414238\theta$; and that of the δ-form, between 1400° and 1604°, is $C_p=0{\cdot}074615 +0{\cdot}0_354752(\theta - 1400) - 0{\cdot}0_53187(\theta - 1000)^2$. The **atomic heat** of the α-form at about 200° is $3R$; at 1000°, 7·184 Cals. per gram-atom, and the value rises to a maximum of 8·25 Cals. The at. ht. of the β-form at 1070° is 6·313 Cals.; and that of the γ-form is 7·722 Cals. at 1400°, rising to 10·3 Cals. per gram-atom at 1500°.

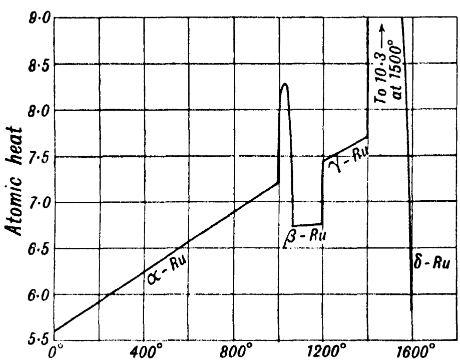

FIG. 1.—The Specific Heat of Ruthenium.

J. L. Byers studied the behaviour of the metal on cupellation. After osmium, ruthenium is considered to be the least fusible of the platinum metals. H. St. C. Deville and H. Debray observed that small quantities can be fused in the top of the oxyhydrogen flame; at the same time, the smell indicates that some metal is volatilized as it is oxidized. A. Joly said that the metal can be readily fused in the electric arc, and to avoid loss by volatilization, the heating should be rapid. A blue superficial film of oxide is formed on the metal. This can be removed by heating it in hydrogen. A. Joly thought that the **melting point** exceeds 1950°. W. R. Mott estimated the m.p. to be 2400°; W. Guertler and M. Pirani, and F. E. Carter, 2450°. T. Carnelley studied the relation between the m.p. and the thermal expansion. According to H. Moissan, the metal volatilizes in the electric arc furnace, and the vapour condenses in droplets which form hopper-shaped cubes, or cubic crystals *en tremies*—**1.** 11, 3. W. Crookes observed a loss of 25 per cent. in 8 hrs. when ruthenium is heated at 1300° in air. This is due to the formation of a volatile oxide. The comparative volatility at 1300° is 100 times that of platinum, and one-fifth that of osmium. W. R. Mott estimated the **boiling point** to be 4500°, but this number is generally considered to be 2000° too high. F. E. Carter gave 2520° for the b.p. J. W. Richards estimated 46 cals. per gram for the **latent heat of fusion**; or 26 kilojoules per gram-atom; and the latent **heat of vaporization,** 10 kilojoules per gram-atom. The **heat of transformation** for the $\alpha \rightleftharpoons \beta$-forms is 0·69 Cal. per gram-atom at 1035°. M. Rabinovitsch studied the glow on heating the finely-divided metal. A. D. van Riemsdijk observed no flashing on cupellation. G. N. Lewis and co-workers calculated 6·8 to 6·9 Cals. for the **entropy** of ruthenium at 25°; E. D. Eastman, by different methods, calculated 6·9 to 7·9 cals. at 25°. R. D. Kleeman estimated the internal

energy and entropy. The subject was studied by W. Herz, K. K. Kelley, and E. Kordes.

F. Fritz suggested the application of ruthenium for filaments in incandescent lamps. Many of the early observations on the **spectrum** of ruthenium are of little value because the ruthenium employed in the work was contaminated with other members of the platinum family. As a consequence, lines attributed to ruthenium belong to other metals of the family—*e.g.* F. McClean,[2] C. E. Gissing, etc. The **spark spectrum** was observed by E. Demarçay, A. Bramley, G. Kail, A. G. Shenstone, L. A. Sommer, W. F. Meggers and co-workers, F. Exner and E. Haschek, W. E. Adeney, and J. M. Eder and E. Valenta. The most intense lines of the spark spectrum are: 2402·80, 2678·80, 2692·18, 2712·49, 2734·41, 2945·79, 2965·70, 2976·70, 3661·58, 3790·71, 3799·02, 3799·48, 4080·82, 4200·09, 4372·40, and 4554·74. E. Demarçay observed that the sparking of soln. of ruthenium salts furnishes a band spectrum. H. A. Rowland and R. R. Tatnall, F. Exner and E. Haschek, J. M. Eder and E. Valenta, and A. Hagenbach and H. Konen observed the **arc spectrum.** The arc spectrum shows a great number of feeble lines; H. Kayser measured 1900 of them. The most intense lines of the arc spectrum are at 3417·50, 3428·50, 3436·87, 3499·09, 3593·18, 3596·31, and 4080·73. According to J. Formanek, the strongest of the green lines in the visible arc spectrum are 5636, 5560, 5511, 5455, and 5401—Fig. 2. The arc spectrum was studied by W. F. Meggers.

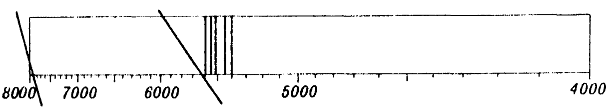

FIG. 2.—Arc Spectrum of Ruthenium.

The **ultra-violet spectrum** was observed by F. Exner and E. Haschek, and G. Kail. W. von Bolton examined the spectrum of the **cathode light** emitted by ruthenium electrodes in electrolyses with strong currents. W. J. Humphreys measured the displacement of the lines by *pressure*; J. E. Purvis, and L. A. Sommer, the effect of a *magnetic field*—the **Zeeman effect**; and J. N. Lockyer enumerated the *enhanced* lines. W. Gerlach and K. Ruthardt discussed the most sensitive lines for the recognition of ruthenium. C. P. Snyder, L. A. Sommer, O. Laporte, E. Paulson, M. Kimura and G. Nakamura, and C. C. Kiess and O. Laporte studied the **structure of the spectrum** and observed many regularities in the frequencies of the lines of ruthenium.

L. H. G. Clark and E. Cohen, and W. F. Meggers and O. Laporte studied the under water **absorption spectrum** of ruthenium vapour. According to E. Formanek, conc., brownish-red, aq. soln. of ruthenium chloride show a red absorption spectrum; light is absorbed in the other parts of the spectrum. With dil. soln., there are absorption bands in the violet, and in the green at about 4925. Ruthenium soln. do not react with alkanna tincture. The absorption spectra of salt soln. were studied by M. Pestemer and P. Bernstein, and R. Samuel and A. R. R. Despande.

The *K*-series of the **X-ray spectrum** of ruthenium was found by S. K. Allison,[3] P. Auger and A. Dauvillier, B. Edlén, D. Coster, A. Leide, F. H. Loring, F. K. Richtmyer and S. Kaufman, P. A. Ross, M. Siegbahn, A. Sommerfeld, E. Wilhelmy, and J. H. Williams to exhibit the lines $\alpha_1\alpha=0·641735$, $\alpha_2\alpha'=0·0646058$, $\beta_1\beta=0·571314$, $\beta_2\gamma=0·560514$, and $\beta_3=0·571930$. M. Siegbahn, E. Friman, and A. Sommerfeld also reported the lines in the *L*-series: $\alpha_1\alpha=4·83567$, $\alpha_2\alpha'=4·84367$, $\alpha_3\alpha''=4·818$, $l\epsilon=5·4864$, $L_{II}=4·1648$, $L_{III}=4·3577$, $\beta_1\beta=4·61100$, $\beta_2\gamma=4·3619$, $\beta_3\psi=4·4767$, $\beta_4\psi=4·5126$, $\beta_6'=4·4764$, $\gamma_1\delta=4·17282$, $\gamma_{2-3}\chi=3·8879$, and $\gamma_5\kappa=4·2766$. Observations on the *L*-series were also made by F. K. and R. D. Richtmyer, F. R. Hirsh and F. K. Richtmyer, J. Zahrednicek, M. J. Druyvesteyn, A. Jönsson, and G. D. van Dyke and G. A. Lindsay. E. Amaldi and co-workers, I. Kurtschatoff and co-workers,

T. H. Newman and H. J. Walke, H. J. Walke, and E. Fermi and co-workers studied the **artificial radioactivity** of ruthenium; H. B. Wahlin, the **emission of positive ions**; and D. Coster and F. P. Mulder, and S. Björek, X-ray levels.

G. L. Locher[4] studied the **photo-electric effect**; T. Pavolini, the photosensitivity; and N. Piltschikoff, the **Moser rays.**

C. Benedicks[5] observed that the **electrical conductivity** of ruthenium is $6{\cdot}9\times10^{-4}$ mho per cm. cube at 18°. F. M. Jäger and E. Rosenbohm observed the following values for the electrical resistance, R ohms, of a wire 0·3 mm. diameter and 17 cms. in length, on a rising temp.:

	660°	780°	790°	850°	865°	910°	970°	1040°	1140°	1230°
R .	0·394	0·475	0·483	0·522	0·533	0·566	0·618	0·693	0·782	0·857

and on a falling temp.:

	1210°	1150°	1100°	1070°	980°	940°	890°	820°	740°	660°
R .	0·854	0·810	0·772	0·734	0·647	0·607	0·563	0·513	0·641	0·410

There is a turning point in the slopes of the two curves between 1000° and 1100°. According to L. P. Cailletet and E. Collardeau, and M. Berthelot, if two silk bags of the spongy metal be arranged with two wires so that the bags of metal can be made anode and cathode whilst immersed in dil. sulphuric acid (1 : 10), and an electric current be passed until the metals in both bags are saturated with gases, then, when the bags of metal are placed in communication, a kind of gas battery is formed which furnishes an electric current for a few seconds. The capacity of the accumulator is increased by press. During the charging of the accumulator, the ruthenium at the anode is attacked, so that a brown liquid is formed in the vicinity of that electrode. J. C. McLennan and co-workers found that the electrical resistance remains high from ordinary temp., down to that of liquid helium; between −268·8° and −270·7°, the conductivity rises sharply, increasing over 100-fold over this short temp. range; below −270·7°, the resistance decreases only slightly as the temp. is lowered, but at 270·96°, the resistance suddenly disappears, and the metal becomes superconducting. A. Schulze, and W. Meissner and B. Voigt studied the resistance at low temp.; P. W. Bridgman, the effect of press.; and F. Simon, the theory of conductivity. C. E. Mendenhall and L. R. Ingersoll observed that small globules of metal on a Nernst's glower move against the current, whereas rhodium, platinum, palladium, and iridium move with the current. R. H. Atkinson studied the electrolytic transfer of ruthenium with fused alkali chlorides as electrolytes; J. A. V. Butler and co-workers, the oxidation potential; and A. Thiel and W. Hammerschmidt, the over-voltage of hydrogen. F. M. Jäger and E. Rosenbohm measured the **thermoelectric force** of purified ruthenium against purified platinum, and found that with the cold junction at 0°, the thermo-electric force, E microvolts, between 400° and 1600°,

	0°	400°	600°	800°	1000°	1200°	1400°	1600°
E .	0	3,867	6,733	10,097	13,951	18,317	22,991	27,978

The data give no evidence of an allotropic change. The results can be represented by $E=6{\cdot}061040\theta+0{\cdot}0112014\theta^2-0{\cdot}0_5 6663\theta^3+0{\cdot}0_8 4664\theta^4-0{\cdot}0_{11}13036\theta^5$; and conversely, $\theta=0{\cdot}0135635E-0{\cdot}0_4 110538E^2+0{\cdot}0_9 7949E^3-0{\cdot}0_{13}29425E^4+0{\cdot}0_{18}4129E^5$. The results agree with those of A. L. Day and R. B. Sosman.

According to the older observers, ruthenium is paramagnetic. M. Owen obtained $0{\cdot}895\times10^{-6}$ mass unit for the **magnetic susceptibility** at room temp. The value increases a little with rise of temp. K. Honda made some observations on the magnetic properties of ruthenium and gave $0{\cdot}56\times10^{-6}$ mass unit. B. Cabrera and A. Dupérier gave $Ru^{\cdots}=1912\times10^{-6}$ c.g.s. units. A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility increases with temp. up to 427°. C. Sadron discussed the magnetic moment of ruthenium. F. H. Loring studied the subject.

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§ 4. The Chemical Properties of Ruthenium

P. M. Niccolini[1] studied the odour of the elements. L. P. Cailletet and E. Collardeau observed that if a current be passed through electrodes of spongy ruthenium in dil. sulphuric acid, until both electrodes are saturated with gases, and the two electrodes then placed in electrical communication, a kind of gas battery is formed. Under atm. press., the discharge lasts a short time, and the duration is increased by press. M. Berthelot studied the subject. E. Müller and K. Schwabe found that of the hydrogen taken up by reduced ruthenium, 100 per cent. is irreversibly absorbed or chemically combined. E. Müller and K. Schwabe studied the subject. A. Gutbier and W. Schieferdecker observed that the absorption isobars, Fig. 3, are linear, and indicate but a slight absorption, although the gas is driven off only by heating the system at 650°. H. Remy and co-workers, K. A. Hofmann, and K. A. Hofmann and O. Schneider observed that the catalytic activity of the platinum metals in the oxidation of hydrogen in the presence of sodium chlorate soln. decreases in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag. C. Claus stated that the affinity of ruthenium for **oxygen** is greater than that of any other metal of the platinum family with the sole exception of osmium.

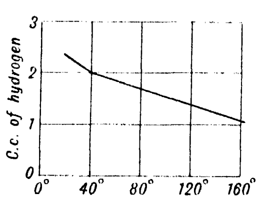

FIG. 3.—Isobars of the System : Ru–H_2.

L. Wöhler and co-workers observed that ruthenium is the most easily oxidized of the platinum metals. According to H. St. C. Deville and H. Debray, and H. Debray and A. Joly, ruthenium is not oxidized by **air** or oxygen at ordinary temp.; but at a bright red-heat, it acquires a blue, superficial film of oxide; when fused in the oxyhydrogen flame, it rapidly oxidizes, and gives off black fumes of oxide which has a smell characteristic of ruthenium tetroxide. F. E. Carter said that if finely divided, the metal begins to oxidize to bluish RuO_2 at 600°, and the oxide is partially decomposed at 1000° into ruthenium and oxygen; in a current of oxygen some ruthenium tetroxide is formed. A. Gutbier and co-workers observed that when finely-divided ruthenium is heated in oxygen, there is a vigorous reaction,

and ruthenium dioxide is formed below 600°; above that temp., the vapour of ruthenium tetroxide is produced, and this decomposes into the dioxide and oxygen below 600°. The previous ignition of ruthenium in hydrogen lowers the speed of oxidation. The fused metal, like platinum, rhodium, iridium, and silver, spits on cooling. F. C. Phillips placed the platinum metals in the order of decreasing catalytic activity: Os, Pd, Pt, Ru, Ir, Rh, and Au in catalyzing the oxidization of hydrogen; and H. Remy and B. Schäffer studied the subject. G. R. Levi studied the effect of ruthenium on the decomposition of **hydrogen peroxide**; and H. Remy and H. Gonnington, the hydrogen-oxygen reaction. E. Leidié and L. Quennessen found that molten **sodium dioxide** oxidizes it to a soluble sodium ruthenate.

H. Moissan observed that powdered ruthenium is attacked by **fluorine** below a red-heat forming a volatile fluoride whose vapour is very dense. O. Ruff said that the attack by fluorine begins at about 300°. A. Joly found that **chlorine** attacks the finely-divided metal at 360°, and O. Ruff said that the attack begins above 200°. The reaction, said A. Joly, is incomplete, but if the metal be mixed with sodium chloride, or if the chlorine be mixed with carbon dioxide, the reaction is quantitative. In the former case, potassium chlororuthenate is formed. H. Remy and T. Wagner found that while chlorine alone attacks ruthenium only partially, with a mixture of chlorine and carbon monoxide, at temp. exceeding redness, the reaction is complete. If the resulting trichloride be reduced to metal, it can be completely chlorinated by chlorine alone, in the absence of carbon monoxide. In agreement with W. Manchot and J. König, it is assumed that the carbon monoxide promotes the reaction by exerting a disintegrating effect on the solid phases. If oxygen be present in the chlorine, the trichloride first formed is converted into the dioxide, but carbon monoxide, by combining with the oxygen, prevents this. C. F. Schönbein found that chlorine water attacks the metal. O. Ruff observed that the metal is attacked by **bromine** between 300° and 700°. C. Claus found that ruthenium is not attacked by **acids,** and **aqua regia** dissolves it very slowly. C. A. Matignon found that **hydrochloric acid** in the presence of oxygen attacks the metal at ordinary temp., and at 125°, in a sealed tube, the attack is complete. A. M. Vasileff observed that, as in the case of platinum, ruthenium black is attacked by hydrochloric acid in air. According to C. F. Schönbein, E. K. Fritzman, E. Leidié and L. Quennessen, and J. L. Howe and F. N. Mercer, the metal is readily attacked by **alkali hypochlorites,** and ruthenium dioxide is formed. J. L. Howe and F. N. Mercer also noted that finely-divided ruthenium is readily soluble in conc. alkaline soln. of hypochlorites, the sodium salt being more effective than the potassium salt, and it is possible to separate ruthenium from the other platinum metals, except osmium, by this means. The hypochlorite oxidizes ruthenium to the tetroxide; and the alkali converts it into ruthenate. W. R. Crowell and co-workers observed the catalytic effect of ruthenium salts on the reduction of **perchloric acid** by hydrogen bromide.

According to H. St. C. Deville and H. Debray, **sulphur** does not unite directly with ruthenium, but if the metal is heated with a mixture of borax and **iron disulphide,** ruthenium sulphide, RuS_2, is formed. G. R. Levi and M. Faldini said that the presence of ruthenium increases the activity of platinum as a catalyst in the oxidation of **sulphur dioxide.** Unlike rhodium, palladium, and iridium, ruthenium is not attacked by fused **potassium hydrosulphate.** M. F. Schurigin, and W. Strecker and M. F. Schurigin observed that ruthenium is attacked by **phosphorus trichloride** at 300°, and also by **phosphorus pentachloride,** with the formation of $Ru_2P_5Cl_{19}$; similarly with **phosphorus pentabromide.** H. Wölbling studied the adsorption of ruthenium by activated **carbon.** L. Mond and co-workers found that ruthenium is attacked by **carbon monoxide** at 300°, under 350 to 450 atm. press. Finely-divided ruthenium acts catalytically on a mixture of air and alcohol, forming aldehyde and acetic acid. F. Fischer and co-workers found ruthenium to be the most active of the platinum metals as a catalyst in reducing

carbon monoxide to methane. K. A. Hofmann and O. Schneider observed that the catalytic activity of the platinum metals in the oxidation of carbon monoxide in the presence of a soln. of sodium chlorate decreases in the order Os, Rh, Au, Pt, Ru, Pd, Ir, Ag. R. Mond observed that at 400 atm. press., and 300°, finely-divided ruthenium forms a non-volatile carbonyl with carbon monoxide. E. Müller and W. Loerpabel studied its action on formic acid. According to C. Claus, when ruthenium is fused with a mixture of **potassium cyanide** and hydroxide, potassium ruthenocyanide is formed. F. C. Phillips noted that ruthenium asbestos favours the oxidation of **hydrocarbons.** G. F. Hüttig and E. Weissberger studied the catalytic decomposition of **methyl alcohol**; and H. St. C. Deville and H. Debray, and E. Müller and co-workers, **formic acid.** J. O. Linde investigated the solubility of ruthenium in **copper.**

P. G. Ehrhardt observed that a **lithium-ruthenium alloy** is harder than ruthenium alone. H. St. C. Deville and H. Debray, and H. Debray prepared a **copper-ruthenium alloy**; W. Truthe studied the behaviour of the **silver-ruthenium alloy** on cupellation, and also of the **gold-ruthenium alloy,** an alloy also investigated by J. O. Linde. H. St. C. Deville and H. Debray observed that ruthenium readily alloys with **zinc,** forming a product which crystallizes in hexagonal prisms; the metal also alloys with tin. The **tin-ruthenium alloys** contain a constituent which crystallizes in cubes—thought to be **ruthenium tristannide,** $RuSn_3$. H. Debray observed that ruthenium dissolves in molten lead. No compound has been detected in the **lead-ruthenium alloys.** The base metal in these cases can be dissolved from the alloys by acids. N. Agéeff and M. Zamotorin studied the diffusion of ruthenium in **iron-ruthenium alloys**; and F. Wever examined the effect of ruthenium on the transition points of iron. H. Remy and H. Gonnington studied the catalytic effect on the hydrogen-oxygen reaction with these alloys and also with the **ruthenium-cobalt alloys,** and the **ruthenium-nickel alloys.** M. M. Goldsmith and W. H. Falck said an alloy of ruthenium 75 per cent., tungsten 17·5 per cent., and nickel 7·5 per cent., is a substitute for osmiridium.

C. Claus found the metal to be oxidized by fused **potassium hydroxide**; and, as shown by U. Antony and A. Lucchesi, the attack is vigorous in the presence of **potassium nitrate,** or **potassium chlorate**; and, as indicated above, it is attacked by sodium dioxide. In each case, alkali ruthenate is formed. E. Tiede and R. Piwonka studied the **alumina** ruthenium phosphors.

Some reactions of analytical interest.—Soln. of ruthenium trichloride when treated with **hydrogen sulphide** give no precipitate at first, but after some time, the liquid becomes azure-blue, and brown ruthenium sulphide mixed with sulphur is precipitated. A dark brown precipitate is produced by **ammonium sulphide,** and it dissolves with difficulty in an excess of the reagent. Black ruthenium hydroxide is precipitated from the soln. by **alkali hydroxides,** the precipitate is soluble in acids but not in alkali lye. When fused with potassium hydroxide, with or without potassium nitrate or chlorate, potassium ruthenate is formed which gives a brown coloration with hydrochloric acid. A soln. of the chloride is first coloured by **zinc** azure-blue, and later, the soln. is decolorized, and ruthenium itself is precipitated. E. Leidié and L. Quennessen observed that **magnesium** also reduces the soln. to metal. In the absence of other platinum metals, **potassium thiocyanate** produces gradually a red, and then a purple, coloration which becomes black when the soln. is heated. W. Singleton [2] recommended the reaction with **thiocarbamide** or **thiocarbanilide** in hydrochloric acid as a test. J. H. Yoe observed that a pink soln. is produced with **ammonium aurintricarboxylate.** Soln. of **potassium iodide** slowly form a black precipitate. A soln. made feebly alkaline with sodium carbonate acquires an orange-yellow colour when treated with **potassium nitrite,** and the liquid becomes carmine-red on adding a little colourless ammonium sulphide; with more ammonium sulphide, ruthenium sulphide is precipitated. According to M. C. Lea, if a drop of ruthenium trichloride is added to an ammoniacal soln. of **sodium thiosulphate,** and the mixture heated

for a few minutes, a purple-red colour is produced. The limits of the test are about 1 part in 100,000 parts of soln. R. Gilchrist obtained a similar result with **thiourea**—L. Tschugaeff's test for osmium. V. N. Ivanoff said that **thiocyanates** do not give a definite precipitate with ruthenium salts. Boiling a soln. of a ruthenium salt with **phloroglucinol,** after the ruthenium soln. has been made alkaline with potassium nitrite, gives a deep violet; **allyl thiourea** gives a blue; and *p*-**nitrosophenol,** a deep violet (S. C. Ogburn); and thiocarbamide, a bluish-green colour (L. Wöhler and L. Metz). Ruthenium tetrachloride is reduced by **hydroxylamine** to the trichloride—*vide* platinum tetrachloride.

Uses.—As indicated above, ruthenium has been suggested as an ingredient for the filament of incandescent lamps,[3] and as indicated below, some salts are employed as stains for histological specimens.

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§ 5. The Atomic Weight and Valency of Ruthenium

Ruthenium behaves as an element, of variable valency. In ruthenium dichloride, the element is *bivalent*, but there is some doubt about the chemical individuality of this salt, and H. Remy[1] added that ruthenocyanic acid is the

only compound in which ruthenium is undoubtedly bivalent. The complex salts of ruthenium trichloride, $2KCl.RuCl_3$, by analogy with the corresponding salts of ferric chloride, are taken to represent *tervalent* ruthenium, and this is also in agreement with the hemitrioxide, Ru_2O_3; the complex salts of ruthenium tetrachloride, $2KCl.RuCl_4$, by analogy with the corresponding osmium and manganese salts, and the dioxide, RuO_2, are taken to represent *quadrivalent* ruthenium. The complex ruthenates, K_2RuO_4, analogous with the ferrates, the manganates and the sulphates, are assumed to correspond with *sexivalent* ruthenium; and the perruthenates, $KRuO_4$, by analogy with potassium permanganate, is taken to represent *septivalent* ruthenium. The volatility of the ruthenium tetroxide, RuO_4, is not in accord with the assumption that any of the oxygen atoms are peroxidized; and accordingly it is assumed that ruthenium has the maximum valency, and like osmium in the tetroxide OsO_4, that ruthenium is *octovalent*. The subject was discussed by H. Kauffmann. E. Zinth and P. Zaimis, T. M. Lowry, W. Manchot and co-workers, and H. Remy obtained indications that *univalent* ruthenium salts may exist. W. Manchot and J. Düsing noted the resemblances between iron and ruthenium in this connection. R. Charonnat said that the valencies of ruthenium range from 1 to 8, and that no salts of ruthenium with a co-ordination number of 4 have been successfully prepared. A. Werner and A. P. Smirnoff showed that the co-ordination number is 6; and R. Charonnat stated that salts with a co-ordination number 6 include $(NH_4)_3[RuCl_6).H_2O$, etc.; and salts with a co-ordination number 8 include $H_4(C_2H_4N_2)[Ru(H_2O)Cl_7]$, and $H_4(C_2H_4N_2)[Ru(OH)Cl_7]$. M. Gerber studied some relations of the at. wts.; and R. Charonnat, and F. H. Burstall, the stereo-chemistry of some ruthenium salts.

The equivalent weight of ruthenium approximates 50, and if this number be doubled for the atomic weight, the result is in accord with (i) the sp. ht. rule; (ii) with the law of isomorphism in the isomorphous series of the dioxides of ruthenium, titanium, and tin, and in the chlororuthenates, K_2RuCl_6, isomorphous with the chloroplatinates, K_2PtCl_6; and (iii) the corresponding position of ruthenium as the first member of the second series of triads in the eighth group in the periodic table. J. W. Mallet placed ruthenium in the arsenic group and represented its at. wt. by 65, about half the value now generally accepted. K. Seubert discussed the subject.

C. Claus' value 103 to 104 for the at. wt. of ruthenium was generally accepted between 1845 and 1890. His main results were based on the analysis of potassium chlororuthenite, K_2RuCl_5, and three series gave 97·09, 103·24, and 107·41 for the at. wt. These values are very discordant, and they are now discarded. A. Joly determined the ratio $Ru : RuO_2$, by reducing the dioxide in hydrogen, and hence calculated 101·668 for the at. wt.; the $Ru : Ru(NO)Cl_3.H_2O$, by reduction in hydrogen, and from the results calculated 101·739; and the ratio $Ru : (NH_4)_2Ru(NO)Cl_5$, also by reduction in hydrogen and so obtained 101·622—general mean=101·661. T. Vogt reduced the dioxide in a current of hydrogen and the average value of six determinations of the ratio $Ru : RuO_2$ was 101·63. The International Committee on Atomic Weights for 1926 give 101·7 as the best representative value.

The **atomic number** of ruthenium is 44. F. Allison and E. J. Murphy [2] observed that ruthenium has two **isotopes,** but F. W. Aston found that there are probably seven isotopes:

Mass	96	98	99	100	101	102	104
Abundance	5	—	12	14	22	30	17 per cent.

giving the calculated at. wt. is 101·1, where the found value is 101·7. E. N. Gapon, and J. H. Bartlett discussed the subject—see palladium. The **electronic structure,** according to the plan of N. Bohr, and E. C. Stoner, is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 4, 6) for the M-shell; (2, 2, 4, 4, 2) for the N-shell; and (2) for the O-shell. E. N. Gapon, H. J. Walke, S. Kato,

W. Hulme-Rothery, H. Lessheim and R. Samuel, G. I. Pokrowsky, C. D. Niven, and P. D. Foote studied the subject. Neither E. Rutherford and J. Chadwick, nor H. Pettersson and G. Kirsch have observed the **atomic disruption** of ruthenium by bombardment with α-rays.

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§ 6. The Ruthenium Oxides

It is an interesting sign of the times that when a new element is discovered, there is a rush from many sides to torture the baby by oxidation, chlorination, fractionation, and so many other appliances which the chemist has at his disposal, yet here, in ruthenium, there is an element of an age exceeding four score years and ten, which is treated with so much respect that it yet awaits the severe ordeal it must inevitably undergo before it can occupy a worthy place in our records. We have read the properties of ruthenium so frequently that we are inclined to give the stereotyped records far more confidence than the evidence justifies.

The venerable observations of C. Claus,[1] H. Debray and A. Joly, H. St. C. Deville and H. Debray, and of E. Frémy on the oxides of ruthenium have been, in part, revised by A. Gutbier and F. Ransohoff, and the results show that a more complete revision is very necessary.

C. Claus said that **ruthenium monoxide,** RuO, can be prepared by strongly heating a mixture of equimolar parts of sodium carbonate and ruthenium dichloride in a current of carbon monoxide, and removing the soluble salts by leaching with water. The dark grey powder is reduced to the metal by heating it in hydrogen. No hydroxide is known, and the oxide is insoluble in acids so that the salts cannot be obtained directly from the oxide. L. Wöhler and co-workers were unable to prepare the monoxide by the direct oxidation of the metal, or by the reduction of the tetroxide in hydrogen. F. Ransohoff, and A. Gutbier and F. Ransohoff showed that in the first place the existence of the dichloride recommended for preparing the monoxide is doubtful, and in the second place all attempts to obtain a compound containing ruthenium and oxygen in the proportions required for the monoxide were unsuccessful, and they concluded that ruthenium monoxide does not exist. C. Kröger studied the dissociation of the oxide. E. Bruchhaus found

that aq. soln. of cæsium aquopentachlororuthenite, when treated with potash lye, furnished a white, unstable precipitate of **ruthenous hydroxide,** $Ru(OH)_2$. W. Manchot and H. Schmid obtained the hydroxide as a dark brown precipitate. G. Lunde studied the X-radiograms. C. Claus prepared **ruthenous tetramminohydroxide,** $[Ru(NH_3)_4](OH)_2$, by the action of silver hydroxide on the corresponding chloride. The reaction was studied by H. Schwarz.

C. Claus observed that when ruthenium is strongly heated in air it acquires a bluish-black film of oxide which is not decomposed at a white-heat, and he stated that *ruthenium sesquioxide*, **ruthenium hemitrioxide,** Ru_2O_3, is obtained by roasting the metal in air at a high temp. He added that if the roasting be continued for a very long time, more oxygen is taken up, but never sufficient to form the dioxide. H. Debray and A. Joly were unable to prepare the sesquioxide, and added that C. Claus' evidence for the existence of this oxide is not admissible; and F. Ransohoff, and A. Gutbier and F. Ransohoff added that no well-defined oxide can be obtained by heating finely-divided and purified ruthenium in air, the product is a mixture of ruthenium and ruthenium dioxide; but if dry ruthenium trihydroxide, $Ru(OH)_3$, be heated in a current of carbon dioxide, it furnishes ruthenium sesquioxide as an unstable, intermediate product, contaminated with traces of alkali originally present in the hydroxide. Observations were made by A. W. Mond.

C. Claus said that **ruthenium trihydroxide,** $Ru(OH)_3$, the hydrate of ruthenium sesquioxide, is formed by precipitating a soln. of ruthenium trichloride by an alkali hydroxide, and washing the product to remove as much alkali as possible—under the best conditions 2 to 3 per cent. may be retained by the precipitate. He also obtained this hydrate as a precipitate by neutralizing potassium ruthenate with nitric acid; and also by heating an aq. soln. of the trichloride whereby, through hydrolysis, the hydrated sesquioxide is precipitated, and hydrochloric acid is set free. F. Krauss and H. Kükenthal prepared what W. R. Crowell and D. M. Yost considered to be a mixture of ter- and quadri-valent ruthenium hydroxide as follows:

Four grms. of ruthenium are fused in a silver crucible with 30 grms. of potassium hydroxide, and 4 grms. of potassium nitrate and heated until the melt is quite fluid. On cooling, the melt is extracted with 200 c.c. of water and the precipitate collected. The precipitate is then stirred with 100 c.c. of alcohol at 40°. The residue recovered either by decantation or filtration is washed with water and dissolved in dilute hydrochloric acid. The resulting soln. is evaporated to dryness on a water-bath and the residue treated with water. To the dark brown soln. potassium hydroxide or alkali carbonate is cautiously added and the ruthenium hydroxide precipitated, the liquid being still slightly acid. The precipitate is collected, washed with water until the filtrate remains clear, drained at a suction pump, and dried. The resulting black compound is free from alkali and chlorine and is the starting material for subsequent preparations.

They prepared the trihydroxide of a high degree of purity by heating, at 120°, in an atm. of nitrogen, the black precipitate obtained by adding alkali lye to a soln. containing the trichloride. According to C. Claus, the finely-divided, amorphous, dark brown powder shows a calorescence—**5.** 33, 10—when heated. Hydrogen reduces it imperfectly at ordinary temp. It is insoluble in alkali lye, but it dissolves in acids, forming brown soln. of salts of tervalent ruthenium.

F. Ransohoff, and A. Gutbier and F. Ransohoff confirmed the results of C. Claus with respect to the first mode of preparation of this hydroxide, but they obtained a different conclusion with respect to the action of nitric acid on potassium ruthenate. H. Debray and A. Joly previously stated that the precipitate is not the trihydroxide but rather a mixture of the hydrated trioxide and dioxide which they represented as a hydrated ruthenium hemiheptoxide, $Ru_2O_5.2H_2O$, and they obtained this product by the action of alcohol on a soln. of potassium ruthenate. A. Gutbier and F. Ransohoff found that the precipitate in both cases, after washing for many days and drying over sulphuric acid, still retained some alkali which was determined as sulphate, and an allowance made. The products varied in com-

position, and when treated with hydrochloric acid, gave a dark brown soln. of ruthenium trichloride, without the evolution of chlorine, and there remained a black residue. Consequently, it was inferred that the precipitate obtained from potassium ruthenate with the composition $Ru_2O_5.2H_2O$ or $Ru(OH)_3$, is a mixture of ruthenium trihydroxide and variable quantities of an undetermined, anhydrous oxide whose nature has not been determined. L. Wöhler and co-workers said that the trihydroxide loses oxygen and water in vacuo, and when dehydrated in carbon dioxide it yields a mixture of the dioxide and metal. Hydrogen dioxide oxidizes the trioxide to the tetrohydroxide.

A. Gutbier and G. Hofmeier prepared **colloidal ruthenium hydroxide** by reducing an aq. soln. of potassium chlororuthenite, K_2PtCl_5, by hydrazine hydrate in the presence of gum arabic which serves as a protective colloid preventing the flocculation of the dispersed hydroxide.

C. Claus prepared **ruthenium dioxide, or ruthenic oxide,** RuO_2, by roasting and igniting the sulphide ; and also by calcining the sulphate. E. Frémy obtained it by alloying osmiridium with zinc, extracting the zinc with acid, and then heating the product in air or oxygen at 1080° to drive off the osmium and ruthenium tetroxides. If the mixed vapours are passed through a heated porcelain tube, the ruthenium dioxide condenses first. H. Debray and A. Joly obtained the dioxide by roasting the ruthenium, and found that after a time the absorption of oxygen proceeds very slowly, and oxidation is incomplete ; the product is powdered and again roasted. The product is indigo-blue, crystalline dioxide. If the amorphous oxide be heated in oxygen or in vacuo crystals are formed. H. St. C. Deville and H. Debray noted that when ruthenium is roasted in oxygen, a sublimate of the dioxide is formed. F. Ransohoff, and A. Gutbier and F. Ransohoff confirmed the formation of the dioxide by roasting the metal in oxygen, and by calcining the sulphate until its weight is constant. A. Gutbier and co-workers found that the oxidation of finely-powdered ruthenium begins at 600°, and the speed of oxidation increases so rapidly with temp. that it is four thousand times as rapid at 1200° as it is at 700°. Crystals of the dioxide may be detected in the sublimate. The previous ignition of the dioxide in hydrogen reduces the speed of oxidation. S. Aoyama prepared the dioxide in bluish-black, lustrous crystals, by heating ammonium chlororuthenate or the product of the action of hydrochloric acid on ruthenium tetroxide in a current of oxygen at a temp. not exceeding 540°. L. Wöhler and co-workers obtained the dioxide by heating ruthenium chloride at 600° to 700° in oxygen. F. Krauss and G. Schrader, and G. Schrader prepared the dioxide by reducing a soln. of ruthenium tetroxide with a 4 per cent. soln. of hydrogen dioxide, and warming the mixture on a water-bath. The product was dried over phosphorus pentoxide in vacuo, powdered, and heated in vacuo to 300°.

The crystals of ruthenium oxide are a deep indigo-blue which, according to H. Debray and A. Joly, are isomorphous with those of cassiterite and rutile. C. F. Rammelsberg, and H. Dufet found that the crystals are ditetragonal bipyramids, with the axial ratio $a:c=1:0.69243$. V. M. Goldschmidt and W. Zachariasen observed that the X-radiogram corresponds with the lattice dimensions $a=4.51$ A., $c=3.11$ A., $a:c=1:0.689$. M. L. Huggins studied the subject. According to H. St. C. Deville and H. Debray, the sp. gr. is 7·2. G. Schrader gave 4·67 for the sp. gr. at 21°/4°, and, after heating the dioxide to 800°, 5·152 at 21°/4°, which makes it appear as if H. St. C. Deville and H. Debray's value is too high. L. Wöhler and co-workers, and V. M. Goldschmidt gave 19·2 for the mol. vol. ; H. St. C. Deville and H. Debray, 18·6 ; and G. Schrader, 26·8. Although formed at a high temp., the dioxide can be decomposed by heat. H. Remy and M. Köhn measured the dissociation press., p mm., of the dioxide at 930° to 950° and found :

	930°	934°	944°	950°
p	32	32	44·5	50 mm.

The dissociation press. is lowered by the presence of finely-divided ruthenium. Thus, for the mol. proportion of ruthenium associated with RuO_2,

Ru . .	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{2}{3}$	1	2
p . .	23·5	32·2	23·5	23·8	22·8	23·5 mm.

The results are virtually independent of the relative proportions of these two substances. This is taken to indicate that a definite lower oxide cannot exist at these temps., but that a series of solid soln. of the metal and its dioxide is formed. L. Wöhler and co-workers said that the vap. press. is 15 mm. at 1000°, and that at a higher temp. the dioxide decomposes into tetroxide and metal. The heat of formation is $(Ru,O_2)=52{\cdot}5$ Cals. M. le Blanc and H. Sachse observed that the electrical conductivity of ruthenium oxide is small; and A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility increases rapidly with temp. H. Debray and A. Joly observed that when ruthenium is heated in oxygen at a temp. above the m.p. of silver (958°), it is entirely converted into crystalline products, and a portion volatilizes and condenses in crystals. If the current of gas be rapid, the odour of ozone or ruthenium tetroxide is perceived, and a certain quantity of the tetroxide can be condensed in a flask cooled by ice. The inside of the tube is lined with ruthenium dioxide and a small quantity of a black substance which seems to contain more oxygen than the dioxide. The products are similar to those obtained when ruthenium tetroxide and nitrogen are passed through a red-hot porcelain tube, and they are distributed in the same manner. The dioxide is found in the cooler parts of the tube, which indicates that the tetroxide formed at about 1000° decomposes at a lower temp. The tetroxide thus serves as a carrier, and, according to P. Duhem, it is in a state of false equilibrium at ordinary temp. At temp. above 1000°, ruthenium dioxide has a considerable dissociation press., and in vacuo it is partially reduced to the metal, a small quantity of the tetroxide being formed. At a bright red-heat, the phenomena are similar. The phenomenon was discussed by P. Duhem. Ruthenium dioxide is reduced by hydrogen at a slightly elevated temp.; it is not attacked by acids; and it dissolves in molten potassium hydroxide, forming the alkali ruthenate.

C. Claus prepared **ruthenium tetrahydroxide,** or **ruthenic hydroxide,** $Ru(OH)_4.3H_2O$, as a gelatinous precipitate, by evaporating a mixed soln. of sodium carbonate and potassium chlororuthenate. The yellowish-brown precipitate adheres tenaciously to alkali, and when heated it loses water at 300°, and at a higher temp. it deflagrates with vivid incandescence—**5.** 33, 10. A. Joly regarded the product as a nitrosyl derivative on the assumption that C. Claus' K_2RuCl_4 is really $Ru(NO)Cl_3.2KCl$. L. Wöhler and co-workers said that when the tetrahydroxide is heated in vacuo below 800°, it forms the dioxide; and that the tetrahydroxide is reduced by hydrogen dioxide, and that the trihydroxide is oxidized to the tetrahydroxide by the same reagent. A. Gutbier and K. Trenkner obtained the hydroxide by treating the sulphate with potassium hydroxide, and observed that it readily forms a **colloidal ruthenic hydroxide.** A. Gutbier and F. Ransohoff were unable to obtain it in a state sufficiently pure for analysis. The hydroxide dissolves in acids to form ruthenic salts; and it dissolves in alkali lye to form a pale yellow soln. The amphoteric oxide also unites with metal oxides to form salts—the **perruthenites.** Thus, according to A. Joly, when barium ruthenate is heated at 440° it forms **barium perruthenite,** $BaRuO_3$. The perruthenites are analogous with the corresponding permanganites, and perosmiamites. The bluish-black residue is insoluble in water, and hydrochloric acid converts it into ruthenium trichloride.

H. Debray and A. Joly reported that an aq. soln. of ruthenium tetroxide decomposes very rapidly at 100°, and that there is formed black scales of **ruthenium tetritaenneaoxide,** Ru_4O_9. F. Ransohoff, and A. Gutbier and F. Ransohoff repeated the experiment, and found that the tetroxide distils off unchanged so that the liquid which remains contains no trace of ruthenium. This is in agreement with the stability and volatility of the tetroxide at 100°.

H. Debray and A. Joly found that if an aq. soln. of ruthenium tetroxide be kept in a closed vessel, it deposits a black precipitate, which, when dried at 100°, corresponds with **ruthenium hemipentoxide,** Ru_2O_5. The undried oxide was considered to be a *dihydrate,* $Ru_2O_5.2H_2O$. H. Remy found that the precipitate of hydrated ruthenous oxide, obtained by adding alkali lye to the blue soln. of reduced chloride, undergoes spontaneous oxidation to form the hemipentoxide, and that the hemipentoxide is also formed by keeping the hydrated tetroxide in a sealed tube for some time. The product in each case contains water. F. Ransohoff, and A. Gutbier and F. Ransohoff repeated the experiments, and found that the aq. soln. becomes colourless in 24 hrs., and that the black amorphous mass, dried over phosphorus pentoxide, contains no trace of ruthenium tetroxide, and it has a variable composition and gives no support to the hypothesis that the hemipentoxide is formed. L. Wöhler and co-workers observed that the hydrated hemipentoxide reported by H. Debray and A. Joly is really the tetrahydroxide. The reduction of the tetroxide and of potassium ruthenate with alcohol gives the dioxide mixed with an explosive organic compound of ruthenium ; and the process recommended by H. Remy yields the sesquioxide mixed with more or less dioxide. The evidence in favour of the chemical individuality of the salts **hyporuthenates** is rather feeble. A. Joly prepared **potassium hyporuthenate,** approximating $K_2O.6Ru_2O_5$, as a black crystalline product, by heating potassium perruthenate to 400°, in vacuo, when a violent decomposition occurs, and maintaining the products at this temp. for a long time. A. Joly and E. Leidié obtained $K_2O.3Ru_2O_5$, by igniting potassium nitritoruthenate at 400°. The black product is attacked with difficulty by hydrochloric acid. Similarly with **sodium hyporuthenate,** $Na_2O.3Ru_2O_5$, obtained by heating sodium perruthenate for a long time at 440°, in vacuo, and washing the product with water to remove sodium oxide and sodium ruthenate.

C. Claus said that **ruthenium trioxide,** RuO_3, is known only in combination with bases as **ruthenates,** R_2RuO_4, and that is a very unstable compound, being easily resolved into oxygen and ruthenic oxide. H. Debray and A. Joly found that the ruthenates are in many ways analogous to the manganates, but the two classes of salt are not isomorphous, and do not have the same proportion of water of crystallization. F. Krauss and H. Kükenthal observed that soln. of potassium ruthenate liberate 3 eq. of iodine from acidic iodide soln., showing that in these compounds the ruthenium is sexivalent. O. Ruff and E. Vidic found that derivatives of ter- and quadrivalent ruthenium are oxidized to the sexivalent form by potassium permanganate in alkaline soln. C. Claus, and U. Antony and A. Lucchesi, prepared **potassium ruthenate,** $K_2RuO_4.2H_2O$, by igniting ruthenium with a mixture of potassium hydroxide with the nitrate or chlorate. H. Debray and A. Joly obtained it by evaporating in vacuo the mother-liquor obtained in preparing the perruthenate from a soln. of ruthenium trioxide in potash lye ; and also by evaporating, at a temp. below 60°, a soln. containing 50 grms. of ruthenium tetroxide, 70 grms. of potassium hydroxide, and 500 grms. of water. H. St. C. Deville and H. Debray said that the crystals of the monohydrate have a greenish lustre, and appear red by transmitted light ; the rhombic prisms have the axial ratios $a:b:c=0·7935:1:1·1973$. The monohydrate does not lose water at 106° in vacuo ; but it becomes anhydrous, without reduction, at 200°, and the anhydrous salt suffers no change in vacuo at 440°. The crystals of the hydrate rapidly alter on exposure to air owing to reduction and form a black deposit ; even after being dried, they absorb moisture and carbon dioxide. F. C. Phillips observed that hydrogen slowly reduces soln. of potassium ruthenate to the metal, and that ethylene acts quickly. According to C. Claus, the salt dissolves in water, forming a deep orange liquid, but the dil. soln. assumes a green colour owing to the formation of perruthenate, and the deposition of what they regarded as $Ru_2O_5.H_2O$—*vide supra.* C. Claus observed that the aq. soln. is neutral, if the alkali and salts employed in its preparation were not in excess.

The soln. has a strong astringent taste like that of tannic acid. It colours organic substances black by coating them with an oxide. Acids added to the soln. precipitate a black oxide which may contain alkali if the soln. has not been completely neutralized by the acid; but if an excess of acid has been added the precipitated oxide contains a little acid. H. Debray and A. Joly observed that dil. acids furnish the hydrate $Ru_2O_5.H_2O$, but with conc. soln. a precipitate of perruthenate of Ru_2O_5 is formed. With hydrochloric acid, *chlorine* is simultaneously evolved. Conversely, the perruthenates change into ruthenates in the presence of alkalies, and the green colour of the perruthenates changes to an orange colour, and oxygen is at the same time evolved. According to L. Brizard, when the metal is attacked by potassium hydroxide and nitrate there is formed a perruthenate which, on contact with water and nitrite, is reduced to ruthenate; and on passing a current of chlorine into a soln. of the ruthenate, perruthenate is formed and the orange liquid becomes green; with an excess of chlorine, some ruthenium tetroxide is volatilized. Aq. ammonia, in a cold soln. of ruthenate, forms a dark brown precipitate which with hydrochloric acid and potassium chloride passes into $Ru_2H_2Cl_3(NO).2KCl.2HCl$. Some reactions were studied by M. C. Lea, and J. L. Howe. L. Wöhler and co-workers said that potassium ruthenate with alcohol forms ruthenium dioxide and an explosive organic compound of ruthenium; and with carbon dioxide, or nitric acid, it forms a mixture of tetroxide, and tetrahydroxide.

F. Krauss prepared **rubidium ruthenate,** Rb_2RuO_4, and its *monohydrate*, $RbRuO_4.H_2O$, by fusing a mixture of ruthenium and a mixture of rubidium hydroxide and nitrate. When a soln. of potassium or rubidium ruthenate is treated with conc. aq. ammonia, there is formed what appears to be **ammonium ruthenate,** $(NH_4)_2RuO_4$, but cæsium ruthenate yields a less well-defined product. The compound is not a true ammonium salt, but rather **ruthenium dioxydihydroxydiammine,** $RuO_2(OH)_2(NH_3)_2$. When a soln. of potassium ruthenate is treated with a 10 per cent. soln. of trimethylamine it forms a precipitate with a composition corresponding with **trimethylammonium ruthenate,** $\{NH(CH_3)_3\}_2RuO_4$. A fused mixture of ruthenium, cæsium hydroxide, and nitrate furnishes **cæsium ruthenate,** Cs_2RuO_4, which can be hydrated to form the *monohydrate*, $Cs_2RuO_4.H_2O$.

H. Debray and A. Joly prepared **sodium ruthenate,** $Na_2RuO_4.2H_2O$, in a manner similar to the potassium salt. The *dihydrate* does not crystallize well, and cannot be readily purified. J. L. Howe and F. N. Mercer obtained the ruthenate by the action of sodium hypochlorite on finely-divided ruthenium. P. Niggli and W. Nowacki discussed the crystal structure of the salts. By adding silver nitrate to a soln. of alkali ruthenate, H. Debray and A. Joly found that the ruthenium is quantitatively precipitated as black **silver ruthenate,** Ag_2RuO_4. A soln. of barium hydroxide dissolves ruthenium tetroxide with the evolution of oxygen, and the formation of a black precipitate which rapidly changes into vermilion-red **barium ruthenate,** $BaRuO_4.H_2O$. The same compound is formed when barium chloride is added to a soln. of potassium ruthenate; with strontium chloride there is formed red **strontium ruthenate,** $SrRuO_4.nH_2O$; with calcium chloride, black **calcium ruthenate,** $CaRuO_4.nH_2O$; and with magnesium chloride, black **magnesium ruthenate,** $MgRuO_4.nH_2O$.

H. St. C. Deville and H. Debray could not isolate **ruthenium hemiheptoxide,** Ru_2O_7, but the salts of *perruthenic anhydride* are known. They obtained **potassium perruthenate,** $KRuO_4$, by passing a current of chlorine through a hot, orange-yellow soln. of potassium ruthenate. If the passage of the gas be discontinued before ruthenium tetroxide is evolved, the green liquid deposits black crystals of the perruthenate. H. Debray and A. Joly gradually added 50 grms. of ruthenium tetroxide, fused under water, to a soln. of 60 grms. of potassium hydroxide in 250 grms. of water at 60°. Oxygen is evolved and the liquid becomes green, and then almost black. When the change is complete, the liquid is allowed to cool in a closed vessel. It deposits small crystals which are drained on porous tiles and

dried in vacuo over a desiccating agent. The opaque, black, lustrous octahedra belong to the tetragonal system, and, according to H. Dufet, have the axial ratio $a : c = 1 : 1{\cdot}6340$. The crystals are not isomorphous with those of potassium permanganate. When the perruthenate is heated to 400°, in vacuo, it decomposes rapidly, forming the ruthenate and ruthenium dioxide. The dry salt does not alter on exposure to dry air, but in moist air it acquires the smell of ruthenium tetroxide. The salt commences to decompose at 210°, and 360°, potassium ruthenate and ruthenium dioxide are rapidly formed with the evolution of oxygen, and ultimately there is produced $K_2O.2Ru_2O_5$—*vide supra*. F. C. Phillips studied the reducing action of hydrogen on a soln. of the salt. According to H. St. C. Deville and H. Debray, the salt dissolves freely in water to form a green soln. which soon decomposes, emitting ruthenium tetroxide, and depositing hydrated hemipentoxide —*vide supra*. Dry chlorine decomposes the perruthenate in the cold, forming potassium chloride and ruthenium tetroxide. F. C. Phillips studied the action of hydrocarbons, carbonyl sulphide, and methyl sulphide and hydrosulphide. Alkali lye transforms the perruthenates into ruthenates. H. Debray and A. Joly prepared **sodium perruthenate,** $NaRuO_4.H_2O$, by a process similar to that employed for the potassium salt. The black, lamellar crystals of the monohydrate are decomposed at 440° with the evolution of water and oxygen, leaving a residue of $Na_2O.3Ru_2O_5$—*vide supra*. The sodium salt is more soluble than the potassium salt in water, and a green soln. is formed.

As indicated in connection with the dioxide, H. St. C. Deville and H. Debray, and A. Gutbier and F. Ransohoff found that **ruthenium tetroxide,** RuO_4, is formed when air or oxygen is passed over ruthenium at a high temp. J. L. Howe and E. A. O'Neal observed that it is formed in the electrolytic oxidation of ruthenium sulphate. In 1860, C. Claus prepared ruthenium tetroxide by passing chlorine through a soln. of alkali ruthenate at 80° to 90°. The tetroxide distils over, and on cooling forms a golden-yellow mass of crystals. J. L. Howe and F. N. Mercer found that ruthenium may be completely distilled as tetroxide from a soln. of potassium ruthenate after treatment with chlorine. The oxide was so obtained by J. L. Howe, and H. Debray and A. Joly.

O. Ruff and E. Vidic recommended preparing the tetroxide of a high degree of purity by distilling at 40° to 50°, in a current of air, an acidified soln. of the mass obtained by fusing in a silver crucible a mixture of 1 part of finely-divided ruthenium, 2 parts of potassium permanganate, and 20 parts of potassium hydroxide. The tetroxide condenses in a receiver, cooled with ice, in the form of long yellow needles.

According to C. Claus, any compound of ruthenium can be converted into the tetroxide by mixing it with a large excess of potassium hydroxide and passing a current of chlorine; and an acidic soln. can be oxidized by a mixture of potassium chlorate and hydrochloric acid. According to J. L. Howe and F. N. Mercer, finely-divided ruthenium is oxidized to the tetroxide by an excess of a soln. of hypochlorite. O. Ruff and E. Vidic observed that ruthenium compounds are oxidized to the tetroxide by a mixture of sulphuric acid and potassium permanganate. According to A. Gutbier, the tetroxide can be purified by repeatedly shaking it with warm water to remove all traces of chlorine, separating the solid as completely as possible from water, and finally subliming it several times in vacuo. H. Debray and A. Joly observed that the oxide can be preserved in tubes freed from organic matter, and dried by heating to redness in a current of dry hydrogen.

The tetroxide forms golden-yellow crystals. H. Debray and A. Joly observed that the vap. density at 100° and 106 mm. press., is 5·77, corresponding with a mol. wt. of 166·7—theory for $RuO_4 = 165{\cdot}2$. G. Schrader, and F. Krauss and G. Schrader gave 3·287 for the sp. gr. at 21°/4°, and 51·4 for the mol. vol. The tetroxide melts by the heat of the hand, for its m.p. is 25·5° It furnishes a deep orange-red liquid which solidifies slowly even when seeded with crystals of the oxide. The fused oxide remains vitreous a long time, and has been obtained in

distinct crystals only by sublimation which readily occurs with a slight change of temp. under a press. of 3 or 4 mm. No b.p. has been observed; it does not boil below 106°, and before boiling occurs the liquid distils rapidly. H. St. C. Deville and H. Debray observed that at about 108° the distillation is so rapid that with a large quantity of liquid a violent explosion occurs with the production of dense, black fumes. H. Debray and A. Joly said that the tetroxide is stable below 106°, but at 107° sudden decomposition takes place with production of a smoky flame, the liquid portion being converted into the crystallized dioxide, whilst a pulverulent form of the same oxide is deposited on the sides of the tube. Decomposition is complete, but there is no actual explosion. As indicated in connection with the dioxide, the vapour of the tetroxide is stable at a very high temp., and it decomposes above 500° into oxygen and ruthenium dioxide. The vap. press. at 108·8° is 183 mm., at 42°, 20 mm., and at 0°, almost zero. The tetroxide can be distilled in water vapour if chlorine or hypochlorous acid be present. According to A. Joly, when thoroughly dried ruthenium tetroxide in sealed tubes is kept in the dark, no alteration takes place, but on exposure to sunlight, the walls of the tube become coated with a pale brown layer, which gradually increases in thickness and eventually transmits only red light. Beyond this point, the tetroxide behind undergoes no further change. The brown deposit dissolves at once in potassium hydroxide soln., forming a yellow liquid without any trace of green, and in hydrochloric acid with evolution of chlorine and formation of a soln. of ruthenium trichloride.

Rubidium tetroxide is soluble in water. The aq. soln., and the solid tetroxide, both possess an odour like that of ozone, but the vapour is not poisonous like that of the corresponding osmium tetroxide. Ruthenium tetroxide dissolves in water, forming a golden-yellow soln. which contains no definite hydrates. The pure soln. may be kept for some time, even in diffused light, but gradually decomposes with evolution of oxygen and deposition of a black layer of the hemitrioxide, Ru_2O_3. The decomposition by water is more rapid the higher is the temp., and at 100° it rapidly becomes complete—brilliant black scales of the lower oxide, $Ru_4O_9.2H_2O$, being obtained—*vide supra*. O. Ruff and E. Vidic said that the aq. soln. of ruthenium tetroxide is not affected by the addition of hydrofluoric acid, but is reduced with the evolution of the halogen when warmed with other halogen acids. A. Joly also found that the halogen hydra-acids transform the tetroxide rapidly into the trichloride, tribromide, or triiodide; in the last case, the reaction proceeds with explosive violence. The reaction is symbolized: $2RuO_4+16HCl=2RuCl_3+5Cl_2+8H_2O$. H. Gall and G. Lehmann said that the product of the reaction is a mixture of ruthenium *tri*- and tetra-chlorides, and not, as supposed by O. Ruff and S. Mugden, H. Remy, S. Aoyama, H. Remy and A. Lührs, and A. Gutbier and K. Trenkner, the trichloride alone (*q.v.*). O. Ruff and E. Vidic found that the tetroxide is rapidly reduced to the tetrachloride when warmed with dil. hydrochloric acid, and that this slowly decomposes into trichloride and chlorine especially when the soln. is boiled to remove the chlorine as it forms. There is a similar reaction with hydrobromic acid, but the second stage, the reduction to tribromide, proceeds more rapidly; with hydriodic acid, black, insoluble ruthenium triiodide is immediately formed. J. L. Howe observed that the vapour of the tetroxide detonates in contact with sulphur. Organic substances reduce the tetroxide very easily, and a black precipitate is deposited on the substance, and hence L. A. Ranvier proposed it as a reagent in the preparation of histological specimens for microscopic examination. It attacks rubber, mastic, and cork. L. Wöhler and co-workers found that when reduced with alcohol the tetroxide forms the dioxide mixed with an explosive organic compound of ruthenium. The reaction was studied by A. Gutbier. J. L. Howe, and A. Gutbier and K. Trenkner found that the solid tetroxide is reduced by alcohol with explosive violence; but in hydrochloric acid soln., alcohol reduces it to the trichloride. H. Debray and A. Joly observed that the tetroxide

attacks mercury. Alkalies, and baryta transform the tetroxide into ruthenates; and the tetroxide dissolves in alkali lye, and the soln. gives a precipitate of finely-divided ruthenium when treated with alcohol. J. L. Howe observed that the tetroxide is covered with water, and then with a conc. soln. of cæsium chloride to which a little hydrochloric acid has been added, the salt $Cs_2RuO_2Cl_4$ is slowly formed; and similarly with rubidium chloride.

F. Krauss showed that ruthenium tetroxide has a weak acidic reaction; and that the oxide in soln. behaves as an electrolyte, being decomposed by the current, forming a green liquid. It forms salts with the alkalies, but only **ammonium perruthenate,** $(NH_4)_2RuO_5$, could be isolated. The salt was obtained by adding conc. aq. ammonia to a conc. aq. soln. of ruthenium tetroxide until the colour changed from yellow to greyish-brown, and then evaporating the soln. A *monohydrate*, and a *dihydrate* were prepared.

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§ 7. The Ruthenium Halides

All four halogens form salts with ruthenium. H. Moissan [1] found that when fluorine acts on red-hot ruthenium, a dense, coloured vapour is formed which was supposed to be **ruthenium difluoride,** RuF_2. O. Ruff observed that the attack begins at 300°. F. Krauss and H. Kükenthal were unable to prepare **ruthenium trifluoride,** RuF_3, by the action of hydrogen fluoride on the trihydroxide. O. Ruff and E. Vidic heated the powdered metal, reduced from the tetroxide, with fluorine at about 280°, and obtained **ruthenium pentafluoride,** RuF_5, as a dark green, transparent mass of sp. gr. 2·963 at 16·3°; mol. vol. 66·38; and the m.p. 101°. The vap. press. at 226° is 173 mm. and the b.p. lies between 270° and 275°. Moisture rapidly decomposes the pentafluoride, forming ruthenium tetroxide and a lower oxide, and hydrofluoric acid, and the colour becomes dark brown, and finally a black gelatinous mass is formed. Liquid water produces a soln. of ruthenium tetroxide and hydrofluoric acid, and a black precipitate of a lower oxide. With iodine vapour, iodine pentafluoride is formed; with conc. hydrochloric acid, chlorine is developed, and a soln. of ruthenium tetrachloride is formed; with dry hydrogen chloride there is no reaction, and with the moist gas, the reaction is incomplete; with sulphur at 300°, there is a vigorous reaction, and sulphur hexafluoride is formed; dry carbon disulphide, benzene, and toluene exert a feeble action; chloroform and carbon tetrachloride have a vigorous action; silicon at a high temp. has no action; copper, and mercury have very little action at ordinary temp., but fluorides are slowly formed at higher temp.; platinum, and gold are not attacked at about 300°; and a soln. of sodium hydroxide produces a hissing noise on contact with the pentafluoride, forming a soln. of ruthenate, and a golden-yellow precipitate accompanied by a small amount of a black precipitate.

Three chlorides have been described—$RuCl_2$, $RuCl_3$, and $RuCl_4$—as well as their complex derivatives.

H. Remy's study of the reduction of soln. of ruthenium trichloride showed that a **ruthenium monochloride,** RuCl, may be formed as an intermediate stage in the reduction of the dichloride to metal by sodium amalgam—*vide infra.* In their study of the direct formation or decomposition of ruthenium trichloride, L. Wöhler and P. Balz obtained no evidence of the formation of a monochloride. On the other hand, by reducing soln. of ruthenium chloride by hydrogen in ultra-violet light, the soln. becomes colourless and then blue. F. Krauss, and E. Bruchhaus showed that the colourless soln. probably contains bivalent ruthenium, and that the blue soln. contains univalent ruthenium. According to C. Claus, ruthenium, at a dull red-heat, is slowly attacked by chlorine, a yellow fume of the highest chloride is first produced and carried forward by the gas. The metal at this stage suffers no change of appearance or perceptible increase in bulk; at a later period, a little trichloride sublimes and the metal turns black, and in the course of 2 hrs. is converted into a black and partly crystalline **ruthenium dichloride,** or **ruthenous chloride,** $RuCl_2$. The conversion may not be complete, and to saturate the metal completely with chlorine, so as to produce the dichloride, it is necessary to pulverize the first product, and repeat the process. K. Trenkner, and A. Gutbier were unable completely to saturate the metal with chlorine, and the results gave less chlorine than corresponds with the theoretical value required for the dichloride. A. Joly inferred that the product is a mixture of ruthenium and its trichloride; and A. Gutbier, that a reversible reaction: $Ru+Cl_2 \rightleftharpoons RuCl_2$ is involved, so that the product is assumed to be a mixture of ruthenium and its dichloride. J. L. Howe and S. C. Ogburn passed a mixture of chlorine and carbon dioxide over heated, finely-divided ruthenium, and obtained a brown powder consisting mainly of ruthenium dichloride. W. Manchot and H. Schmid obtained it by the cathodic reduction of the trichloride. F. Krauss and H. Kükenthal obtained similar results at 360°, and found that the prolonged action of the chlorine yields Ru_2Cl_5. H. Gall and G. Lehmann found that when ruthenium trichloride

is reduced in alcoholic soln. by hydrogen in the presence of spongy platinum, ruthenium dichloride is formed along with some ruthenium, the production of the metal is prevented by adding hydrochloric acid, preferably derived from chloroform, to the alcoholic soln. The dichloride behaves as a reducing agent. The soln. does not absorb carbon monoxide at atm. temp.; but at 210°, it forms $RuCl_2.2CO$—*vide infra.* L. Pauling, V. M. Goldschmidt, and G. Bruni and A. Ferrari discussed the possible structure of the space-lattice of the dichloride. C. Claus observed that the dichloride so obtained is insoluble in water and acids, although water may extract a trace of ruthenium trichloride. A soln. of potassium hydroxide acts like water even when the mixture is evaporated to dryness. If this dry residue be washed with water, and digested with hydrochloric acid, a little oxide is dissolved, and the acid acquires the colour of the trichloride. F. Krauss and E. Bruchhaus obtained bivalent compounds by the simultaneous action of hydrogen and exposure to short wave radiation. J. L. Howe and S. C. Ogburn found that the dichloride they prepared is insoluble in most solvents but is readily soluble in absolute alcohol, forming a blue soln. like that produced by the action of reducing agents on ruthenium trichloride. The soln. is slightly ionized, but is not colloidal.

Nearly forty years before the discovery of ruthenium by C. Claus, L. N. Vauquelin had observed an azure-blue soln. is obtained by the reducing action of zinc on certain soln. of the platinum metals. This coloration was attributed to the presence of osmium, but the reaction is now known to be characteristic of ruthenium trichloride. C. Claus observed that when hydrogen sulphide is passed through a soln. of ruthenium trichloride, a dark brown sulphide is precipitated, and the liquid acquires a blue colour. After expelling the hydrogen sulphide from the liquid by passing a current of air, the azure-blue liquid which remains contains ruthenous chloride and hydrochloric acid. A. Joly, and J. L. Howe agreed. C. Claus' argument was (i) hydrogen sulphide is known to reduce soln. of the chlorides of other platinum metals; (ii) the sulphide precipitated by the hydrogen sulphide contains 2 or more gram-atoms of sulphur to 1 gram-atom of metal; (iii) the trichloride is coloured blue by other reducing agents—*e.g.* zinc; and (iv) when a soln. of trichloride is evaporated and the residue heated, it turns green, but shows isolated blue spots. The dichloride cannot be so obtained because a basic salt is produced. When the blue soln. is treated with alkali lye, ruthenium sesquioxide is precipitated, just as when a soln. of a lower chloride of iridium is similarly treated, hydrated iridium dioxide is formed. H. Remy added that (v) a cold soln. of sodium hydroxide gives a brown coloration which, if the soln. are conc., becomes a brown precipitate, soluble in hydrochloric acid to form a blue soln., but if only a trace of air is admitted the soln. is green; hot soln. of sodium hydroxide give a dark brown precipitate which is soluble in 10 per cent. hydrochloric acid with the formation of a yellowish-brown soln.; and (vi) ammonia gives a greyish-black precipitate soluble in hydrochloric acid to a blue soln. and soluble in excess of ammonia to a dark violet soln.; hot ammonium carbonate gives a dark green coloration; iodine soln. are decolorized in the presence of acid. C. Claus added that aq. ammonia produces with the blue soln. a violet-blue precipitate which turns green, and with the green soln. it produces a green precipitate and a red liquid. When either the green or the blue soln. is heated with nitric acid, it acquires the orange-yellow colour characteristic of the trichloride. Sulphurous acid and hydrochloric acid decolorize the blue liquor. H. Remy said that all the reactions of soln. of bivalent ruthenium indicate that the compounds of bivalent ruthenium are excessively unstable. S. Aoyama found that when ammonia is added to the product of the action of hydrogen chloride on ruthenium tetroxide, there is a sequence of colour changes with the ultimate formation of a violet compound, **ruthenium diaquotriamminodichloride,** $Ru(NH_3)_3(H_2O)_2Cl_2$. C. Claus prepared **ruthenous tetramminochloride,** $[Ru(NH_3)_4]Cl_2$, by the action of a boiling soln. of sodium carbonate and ammonia on ammonium chlororuthenate.

The reaction was studied by H. Schwarz. According to M. F. Schurigen, and W. Strecker and M. F. Schurigen, phosphorus pentachloride acts on spongy ruthenium to form a complex **ruthenium phosphochloride,** $2RuCl_2.5PCl_3$. W. Manchot and J. König could not prepare **ruthenium carbonyl dichloride,** $Ru(CO)_2Cl_2$, reported by H. Gall and G. Lehmann, and H. Remy; but W. Manchot said that the chloride sublimes as a chlorocarbonyl when heated in carbon monoxide.

H. Remy triturated soln. of ruthenium trichloride with dil. sodium hydroxide in an atm. of carbon dioxide until the sepia-brown colour changed to clear blue, and found that some ruthenium was at the same time precipitated. The results indicate that in the blue soln., most of the ruthenium is present in a bivalent condition, but the complete conversion is impossible without at the same time reducing some to the metallic state. H. Remy and T. Wagner observed that during the reduction of ruthenium trichloride in hydrochloric acid soln. by sodium amalgam, a green coloration is observed between the initial sepia-brown and ultimate dark blue, which is more pronounced as the acidity of the soln. is increased. This point corresponds with the absorption of one equivalent of hydrogen for each ruthenium ion (when allowance is made for the quantity used in the subsidiary reduction of trichloride to metal), and thus points to the existence of the dichloride in soln. H. Remy added that it is possible that some univalent ruthenium chloride is formed, and T. Wagner, and H. Remy and T. Wagner observed that the further addition of sodium amalgam causes the production of dark blue ruthenium monochloride, the reaction being incomplete in strongly acidic soln., but quantitative in more feebly acidic soln. It thus appears that bivalent ruthenium as the free ion and in weak complexes is very unstable and readily passes into the univalent condition, and that ruthenium dichloride, in itself colourless or feebly coloured, gives a dark green additive compound with hydrochloric acid. E. Zintl and P. Zaimis titrated the soln. of ruthenium trichloride with soln. of chromous sulphate and with titanous sulphate, and found that the results confirmed the conclusion that the blue colour of the soln. is due to the univalent metal. E. Bruchhaus showed that when a soln. of ruthenium trichloride is reduced by hydrogen in ultra-violet light, the colourless liquid first formed probably contains bivalent ruthenium, and that the subsequent production of a blue liquid is due to the reduction of the dichloride to monochloride.

R. Charonnat observed that a soln. of ruthenium trichloride which has been warmed contains a preponderating proportion of ruthenium hydroxytrichloride, and of the tetrachloride when prepared cold. When the hydroxytrichloride is heated, in the presence of hydrochloric acid, the trichloride is re-formed; $2HCl + 2Ru(OH)Cl_3 \rightarrow 2RuCl_3 + Cl_2 + 2H_2O$. When ruthenium tetrachloride is reduced with alcohol in the presence of hydrochloric acid, **ruthenium hydrotetrachloride,** $RuCl_3.HCl.2H_2O$, is formed in red, acicular crystals, which when heated lose hydrogen chloride and water, though the water is not all expelled at 200°. If the ruthenium tetrachloride be reduced by alcohol in the absence of hydrochloric acid, a green isomer, $RuCl_3.HCl.2H_2O$, is formed.

According to A. Lührs, and H. Remy and A. Lührs, the fact that when a soln. of ruthenium trichloride, or a soln. of potassium β-chloroperruthenite, is titrated with sodium amalgam, it requires exactly one eq. of hydrogen to produce a blue of maximum intensity, showing that tervalent ruthenium is present; on the other hand, the compound formed by the action of hydrochloric acid on ruthenium tetroxide requires two eq. of hydrogen to develop a blue colour of maximum intensity, and hence it is thought that this salt contains quadrivalent ruthenium. The salt, **potassium oxychloroperruthenite,** $K_4[Ru_2OCl_{10}]$, is readily prepared from the aq. soln., and it is supposed to correspond with brown potassium α-chloroperruthenite—*vide infra.* R. Charonnat doubted the existence of the salt, $K_4[Ru_2OCl_{10}]$. It follows that this compound, which likewise contains quadrivalent ruthenium, replaces the previous so-called "brown or α-pentachlororuthenates." The blue soln. obtained by the complete reduction of ruthe-

nium salts by sodium amalgam contain the bivalent metal. The green coloration, formed intermediately during the reduction exclusively of quadrivalent ruthenium salts in soln. strongly acidified with hydrochloric acid, is due to compounds of tervalent ruthenium. H. Gall and G. Lehmann believe that the product obtained by the action of hydrochloric acid on ruthenium tetroxide is a mixture of the tri- and tetra-chlorides. The green colour of soln. of ruthenium chloride is attributed by H. Remy and co-workers to the presence of tervalent metal, but since soln. of the tervalent metal are sepia-brown, the green soln. would indicate the presence of an isomeric form of the trichloride. This inference is not justified by the known facts. The green colour is due to the admixture of brown and blue soln. S. Aoyama also inferred that the product of the action of hydrogen chloride on ruthenium tetroxide contains both the chlororuthenates and chloroperruthenites formed by the reactions : $RuO_4+6HCl_{gas}=H_2RuO_2Cl_4+Cl_2+2H_2O$; followed by $H_2RuO_2Cl_4+4HCl=H_2RuCl_6+Cl_2+2H_2O$, and by $2H_2RuCl_6 \rightleftharpoons 2H_2RuCl_5+Cl_2$. H. Remy, and H. Gall also said that the product contains quadrivalent ruthenium, and F. Krauss, that the ruthenium is nearly all in the tervalent state. F. Krauss and H. Kükenthal said that if the tetroxide be treated with hydrochloric acid and potassium iodide, the iodine liberated corresponds with a decrease in valency of 5 in the tetroxide; the reduced soln. furnishes salts of the type R_2RuCl_5, $RuCl_3$, and $Ru(OH)_3$, showing that the metal is here tervalent, and octovalent in the tetroxide. M. Buividaite prepared **ammonium chlororuthenite,** $NH_4RuCl_4.2H_2O$, by reducing the corresponding ruthenate with stannous chloride. The salt loses water at 220° to 230°, and ammonia at 230°. Three only of the chlorine atoms can be removed from the aquo-salt by silver nitrate.

J. L. Howe did not isolate the dichloride, but he reduced a soln. of the trichloride electrolytically, and immediately added cæsium chloride to the blue liquor, and obtained a dark greenish-blue, or olive-green precipitate of **cæsium chlororuthenite,** $3CsCl.2RuCl_2.2H_2O$. The salt oxidizes with great rapidity on exposure to air. E. Bruchhaus treated the colourless soln., obtained by reducing a soln. of ruthenium trichloride by hydrogen in ultra-violet light, with cæsium chloride, and obtained the chlororuthenite, $Cs_3[RuCl_5H_2O]$. M. Buividaite prepared the cæsium salt, $CsRuCl_4.5H_2O$, and **rubidium chlororuthenite,** $RbRuCl_4.4H_2O$, by adding cæsium or rubidium chloride to a soln. of ammonium chlororuthenite. These salts are stable aquo-salts. The cæsium salt loses a mol. of water at 100°. O. W. Gibbs reported **ruthenium hexamminochloromercurate,** $[Ru(NH_3)_4]Cl_2.HgCl_2$.

F. Krauss and H. Kükenthal observed that the prolonged action of chlorine and carbon monoxide at 360° on finely-divided ruthenium furnishes **ruthenium hemipentachloride,** Ru_2Cl_5. The soln. in dil. alcohol is blue or violet, and reacts only slowly with hydrogen sulphide, potassium hydroxide, and silver nitrate, showing that a complex salt is probably formed. C. Claus dissolved ruthenium sesquioxide in hydrochloric acid, and evaporated the soln. to dryness to obtain **ruthenium trichloride,** $RuCl_3$. W. R. Crowell and D. M. Yost found that soln. of ruthenium compounds in hydrochloric acid are reduced by potassium iodide to the tervalent state. L. Wöhler and P. Balz obtained only the trichloride by the action of chlorine on finely-divided ruthenium between 380° and 420°; and L. Wöhler and co-workers, by heating the chloroperruthenite in hydrogen at 400°. A. Joly heated ruthenium in chlorine, and found that the transformation to trichloride is incomplete, but if the chlorine be mixed with carbon monoxide, chlorination readily occurs at 350°. L. Wöhler and P. Balz worked at 400°. A. Joly, K. Trenkner, and A. Gutbier and K. Trenkner obtained the trichloride by warming ruthenium tetroxide with conc. hydrochloric acid on a water-bath; $2RuO_4+16HCl=2RuCl_3+5Cl_2+8H_2O$. A. Gutbier observed that if the reaction is slow to begin, it can be started by the addition of a few drops of alcohol; and he recommended allowing a mixture of ruthenium tetroxide with 20 per cent. hydrochloric acid to stand under reduced press. for a couple of hours. The soln.

was free from chlorine and unconverted oxide, and was concentrated to a syrup by passing air over the warm liquid. When the product was confined over sulphuric acid in an evacuated desiccator, it furnished a black, crystalline mass of the trichloride. The trichloride is also produced when the tetroxide is dissolved in chlorine water, and the soln. evaporated. A mass of crystals of the trichloride remains. F. Krauss and H. Kükenthal obtained the trichloride by the interaction of the vapour of ruthenium tetroxide and dry hydrogen chloride at 105° to 115°—the dark brown, deliquescent mass is of a high degree of purity—and also by the action of dry hydrogen chloride at 105° on the purified trioxide. V. Ipatéeff studied the action of hydrogen under press. According to H. Remy and T. Wagner, ordinary ruthenium is only partially attacked by chlorine, but, in the presence of carbon monoxide, and at temp. above red-heat, the reaction is complete, and the trichloride is formed. J. L. Howe obtained reddish-brown soln. of **chloroperruthenous acid,** H_2RuCl_5, by covering ruthenium tetroxide with conc. hydrochloric acid. L. A. Welo and K. Baudisch studied the magnetic properties.

The trichloride prepared in the dry way by A. Joly furnished a brown powder which is not deliquescent, and is insoluble in cold water. Boiling water acquires a blue colour, which changes to green, and finally decolorizes as a black oxychloride is precipitated and a soln. of hydrochloric acid is formed. The trichloride prepared in the wet way furnishes a mass of black crystals. P. Vinassa discussed the mol. vol. H. Remy and M. Köhn measured the dissociation press., p mm., of ruthenium trichloride between 689° and 841°, and found:

	720°	742°	776°	816°	832°	841°	855°
p .	138	187	288	562	673·5	727	over 800 mm.

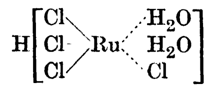
The results show that it decomposes directly into its elements without the formation of intermediate lower chlorides. L. Wöhler and P. Balz came to the same conclusion; they added that the salt decomposes into its elements at 845°, and that the vap. press. measurements are unsatisfactory above 700° owing to the volatility of the trichloride. They gave:

	450°	510°	620°	700°	740°
p	24	30	68	187	389 mm.

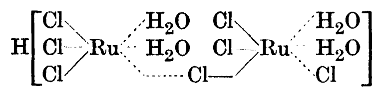
The heat of formation is $(Ru,1\frac{1}{2}Cl_2)=63$ Cals. S. M. Karim and R. Samuel, and M. Pestemer and P. Bernstein studied the absorption spectrum. B. Cabrera and H. Fahlenbrach, and A. N. Guthrie and L. T. Bourland studied the magnetic properties. W. Manchot and G. Lehmann observed that in nitrogen at 270° no chlorine is evolved, but in carbon monoxide, traces of phosgene are formed. The trichloride was found to be insoluble in ether, but it forms a green soln. with absolute alcohol, and this soln. conducts electricity with the evolution of hydrogen at the cathode. The aq. soln. is a good conductor, evolving hydrogen and chlorine with the deposition of the hydroxide, $Ru(OH)_3$. The trichloride is hygroscopic, and is readily soluble in water, and in alcohol. The conc. aq. soln. is brown, but when dilute, it is orange-yellow. The salt has great tinctorial power in aq. soln. The soln. is very sensitive to a rise in temp. and hydrolyzes at 50° to form black hydrated oxide or oxychloride and hydrochloric acid. The colour of the precipitate is so intense that a soln. with 1 part of metal in 100,000 parts of water becomes perceptibly darker. A. Joly reported that if the aq. soln. be evaporated to a syrupy mass, on cooling, it solidifies to a reddish-brown mass of **ruthenium hydrotetrachloride,** $2RuCl_3.HCl.H_2O$, and when gently heated it forms a black mass of the $2RuCl_3.3H_2O$, which yields a brown soln. with cold water.

R. Charonnat prepared **hydrochloroperruthenous acid,** $RuCl_3.HCl.2H_2O$, or $HRuCl_4.2H_2O$, or $H[RuCl_4].2H_2O$, analogous with the corresponding $HFeCl_4.2H_2O$, $HAuCl_4$, and $HIrCl_4.nH_2O$, by boiling a hydrochloric acid soln. of ruthenium tetrachloride and alcohol, and evaporating in vacuo over sulphuric acid and calcium oxide. The acid forms deep red, deliquescent, acicular crystals very soluble in

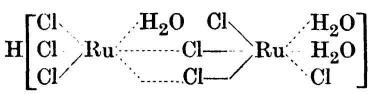
water. When the red acid is heated in a current of carbon dioxide, hydrogen chloride and water, but not chlorine, come off towards 120° leaving $RuCl_3$. If the dil. soln. of ruthenium tetrachloride be reduced by alcohol and evaporated on a water-bath until a surface skin is formed on the liquid, and the product treated with alcohol and again evaporated, the red colour of the liquid changes to green after a few treatments, and, on evaporation in vacuo, as in the case of the red soln., dark green spangles are formed which are soluble in water. This product is a hygroscopic, green isomeric form of the red acid, $RuCl_3.HCl.2H_2O$. R. Charonnat considers that the red and green forms of this acid are cis- and trans-forms of **diaquochloroperruthenous acid,** $H[RuCl_4(H_2O)_2]$:

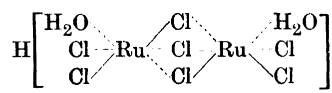


When a mol. of hydrogen is expelled by heat, the co-ordination number 6 can be maintained only by the simultaneous entry of a mol. of the primitive acid into the complex to form the condensation product:



When a mol. of water is expelled the co-ordination number can be preserved without forming a new condensation product; and similarly with a second mol. of water which is also attended by a re-arrangement within the complex:





F. C. Phillips observed that the reduction of ruthenium trichloride by hydrogen begins at about 190°. A. Joly found that when the hydrated salt is heated in a current of hydrogen chloride, it forms the anhydrous chloride. F. Krauss and H. Kükenthal observed that the salt is very hygroscopic, forming a dark red mass. It forms a brown soln. with water. The brown soln. in hydrochloric acid becomes red when boiled. C. Claus found that hydrogen sulphide reduces the aq. soln. to the lower chloride, and at the same time the orange-yellow soln. becomes azure-blue, and a dark brown precipitate is formed; a similar precipitate is produced when the soln. of the trichloride is treated with ammonium sulphide, and it is not perceptibly soluble in an excess of the reagent. The orange-yellow soln. is slowly decolorized by sulphurous acid. G. Sailer observed that sodium hyposulphite forms a sodium sulphitoruthenite. F. Krauss and H. Kükenthal noted that it forms a brown soln. with aq. ammonia. A. Joly found that ruthenium trichloride readily absorbs dry ammonia to form a dark violet **ruthenium hemiheptamminohexachloride,** $2RuCl_3.7NH_3$. Heat is liberated during the absorption of the ammonia, and the reaction is complete at 0°. The ammine forms a bright red soln. with water. This compound forms a violet-red, aq. soln. from which the hydroxyl compound, $Ru_2Cl_4(OH)_2.7NH_3.3H_2O$, is produced, and the hydroxyl compound obtained by the action of ruthenium chloride in aq. ammonia is called *ruthenium red.* It dyes animal fibres a red colour, and with conc. hydrochloric acid, it forms $Ru_2Cl_4(OH)_2.7NH_3.HCl.3H_2O$.

According to G. T. Morgan and F. H. Burstall, ruthenium trichloride absorbs ammonia, yielding a mixture of ammines including probably **ruthenium hexamminotrichloride,** $[Ru(NH_3)_6]Cl_3$, analogous to the ferric chloride derivative, $[Fe(NH_3)_6]Cl_3$, studied by G. F. Hüttig, F. Ephraim and S. Millmann, and W. Biltz and E. Birk. The mixture dissolves in water to form a purple-red soln. of ruthenium red.

Ruthenium red is probably hydrated **ruthenium hydroxychlorotetrammino-chloride,** $[Ru(OH)Cl(NH_3)_4]Cl.H_2O$, which with hydrochloric acid forms **ruthenium dichlorotetramminochloride,** $[RuCl_2(NH_3)_4]Cl.2H_2O$; and with nitric acid, **ruthenium chloronitratotetramminonitrate,** $[Ru(NO_3)Cl(NH_3)_4]NO_3.4H_2O$, which does not react with silver nitrate except on warming. An aq. soln. of ruthenium red with potassium bromide forms **ruthenium hydroxybromotetramminobromide,** $[Ru(OH)Br(NH_3)_4]Br.H_2O$, with hydrobromic acid, **ruthenium dibromotetram-minobromide,** $[RuBr_2(NH_3)_4]Br.H_2O$; with an aq. soln. of potassium iodide, successively **ruthenium hydroxychlorotetramminoiodide,** $[Ru(OH)Cl(NH_3)_4]I$, **ruthenium hydroxyiodotetramminoiodide,** $[Ru(OH)I(NH_3)_4]I$; and ultimately **ruthenium diiodotetramminoiodide,** $[RuI_2(NH_3)_4]I$; and with potassium nitroso-ruthenite, it yields a complex salt, $[Ru(OH)Cl(NH_3)_4]_2Ru(NO)Cl_5$.

There are analogues of the ammines, thus, with ethylenediamine it forms **ruthenium chlorobisethylenediaminochloride,** $[RuCl_2en_2]Cl$; **ruthenium hydroxy-chlorobisethylenediaminochloride,** $[Ru(OH)Cl\ en_2]Cl$, and **ruthenium hydroxy-iodobisethylenediaminoiodide,** $[Ru(OH)I\ en_2]I$; with pyridine, **ruthenium hydroxychlorotetrapyridinechloride,** $[Ru(OH)Cl\ py_4]Cl$, and **ruthenium dichloro-tetrapyridinechloride,** $[RuCl_2py_4]Cl$; and with ethylamine, **ruthenium dichloro-quaterethylaminochloride,** $[RuCl_2(C_2H_5.NH_2]_4]Cl$, and **ruthenium hydroxychloro-quaterethylaminochloride,** $[Ru(OH)Cl(C_2H_5NH_2)_4]Cl$.

L. Wöhler and P. Balz said that the blue colour produced by treating the trichloride with dil. alcohol is probably due to the reduction of the trichloride to dichloride. According to C. Claus, a soln. of the salt gives a precipitate with sodium phosphate. W. Manchot and G. Lehmann observed that when heated in carbon monoxide, some carbonyl chloride is formed; and W. Manchot, that when the chloride is heated in carbon monoxide, a dichloro-carbonyl is formed. W. Manchot and J. König found that aq. or alcoholic soln. of ruthenium trichloride absorb carbon monoxide slowly, but the dry trichloride at 270° absorbs the gas slowly with the incomplete formation of **ruthenium dicarbonyldichloride,** $RuCl_2(CO)_2$. The acceleration of the chlorination of ruthenium at 270° by mixing the chlorine with carbon monoxide depends on the formation of this compound and its decomposition with the production of finely-divided ruthenium. L. Brizard, and J. L. Howe prepared **ruthenium nitrosyltrichloride,** $Ru(NO)Cl_3$, the *monohydrate*, and the *pentahydrate*. F. C. Phillips observed that an aq. soln. of the chloride is bleached by ethylene, but no metal is precipitated. F. Krauss and H. Kükenthal observed that it forms a reddish-brown soln. with alcohol; and the brown soln. with potassium cyanide becomes yellowish-green when boiled. A. Joly observed that the soln. of the chloride in absolute alcohol is purple-violet, but in presence of atm. moisture, or, if the alcohol is not quite anhydrous, the soln. very slowly becomes violet-blue and afterwards deep indigo-blue. The change takes place more rapidly at 60°, and is due to the formation of **hydroxychloride,** $RuCl_2.OH$, which is obtained as a black product when the alcohol is distilled off, and is stable at 150°. It is very soluble in water, forming a deep indigo-blue soln., which gradually deposits ruthenium hydroxide, $Ru(OH)_3$. If the hydroxychloride is dissolved in a considerable excess of hydrochloric acid, it forms a brown soln. of a hydrochloride, which is stable at about 150°, but at 200° is converted into the anhydrous chloride. The hydroxychloride combines with ammonia and forms a compound very soluble in water; it yields an intense crimson soln., turning to yellow in presence of hydrochloric acid. According to C. Claus, sodium formate decolorizes the soln. but does not precipitate the metal; oxalic acid acts similarly; potassium ferrocyanide first decolorizes the soln. and then turns it blue; mercury cyanide colours the soln. blue, and deposits a blue precipitate; and zinc reduces the orange-yellow soln. to the blue lower chloride. When the soln. is treated with an alkali hydroxide or carbonate, a dark brown precipitate of the hydrated sesqui-oxide is formed, soluble in excess. Conc. soln. of the trichloride give with ammonium or potassium chloride, a dark brown, crystalline precipitate. When the

soln. of trichloride is treated with silver nitrate, there is formed a black precipitate which turns white and the soln. at the same time becomes rose-red. The black precipitate is a mixture of silver chloride and hydrated ruthenium sesquioxide; in the course of 24 hrs., the hydrated ruthenium oxide dissolves in the liberated nitric acid, and forms a red soln. whilst the silver chloride remains as a white residue. When aq. ammonia is added to the mixture, the silver chloride dissolves, and black ruthenium sesquioxide is deposited. F. G. Mann and W. J. Pope prepared **ruthenium chloro-$\beta\beta'\beta''$-triaminotriethyleneamine,** $2RuCl_3.N(C_2H_4.NH_2)_3.4HCl.2H_2O$. F. C. Phillips studied the action of hydrocarbons on the trichloride.

Ruthenium trichloride forms a series of complex salts of the type R_2RuCl_5, that is $2RCl.RuCl_3$, and they are usually called *ruthenochlorides* of *chlororuthenites.* The latter term is applied to double salts of the lower chloride, so that these salts are here called **chloroperruthenites.** P. Niggli and W. Nowacki discussed the crystal structure. C. Claus prepared **ammonium chloroperruthenite,** $(NH_4)_2RuCl_5$, by adding ammonium chloride to a conc. soln. of ruthenium trichloride, and evaporating the liquid with small additions of nitric acid. The brown crystalline powder consists of small, transparent, orange-yellow cubes. The salt dissolves sparingly in water, and crystallizes with difficulty from the conc. soln. F. Mylius and A. Mazzucchelli also prepared the salt, but not so A. Gutbier. V. Ipatéeff studied the action of hydrogen under press.; and V. Ipatéeff and O. E. Zvjaginstzeff examined the effect of hydrogen under press. on the ammonium, potassium, and sodium pentachloroperruthenites, and on hydrodihydroxytetrachlororuthenic acid, $H_2Ru(OH)_2Cl_4$, in dil. aq. soln. acidified with hydrochloric acid. The same products are formed in all cases. Reduction is slow at 25° and 20 atm., the soln. is decolorized and a slimy, black precipitate of ruthenium hydroxide is formed, and it is gradually redissolved at atm. press. At 85° and 65 atm., a heavy, black precipitate of the hydroxide is formed; at 160° and 80 atm., a mixture of ruthenium oxide and hydroxide is precipitated; and at 350° and 125 atm., a mixture of ruthenium and its oxide is formed. C. Claus prepared **potassium chloroperruthenite,** K_2RuCl_5, by the action of fused potassium chloride and nitrate on the metal until all is in soln. The green mass becomes orange-yellow when cold. It is dissolved in water, and treated with conc. hydrochloric acid until the precipitate first formed is redissolved. The excess of potassium chloride and nitrate are deposited as the soln. is evaporated, the liquid is then evaporated to dryness, and the dry mass extracted with a little cold water, and the salt purified by recrystallization. U. Antony and A. Lucchesi employed a similar process. R. Charonnat obtained it by the action of hydrochloric acid on potassium oxalatoperruthenite, and S. Aoyama by the action of dry hydrogen chloride on potassium chlororuthenate at 450° to 560°. A. Joly, and J. L. Howe showed that the chloroperruthenite first prepared by C. Claus was probably a nitrosyl salt, $K_2Ru(NO)Cl_5$. L. Brizard obtained the chloroperruthenite by reducing ruthenium nitrosyltrihydroxide with formaldehyde in a boiling alkaline soln., dissolving the precipitate in conc. hydrochloric acid, and separating out the salt in brown crystals by the addition of potassium chloride. S. C. Lind and F. W. Bliss prepared the salt by digesting on a water-bath a mixture of freshly distilled ruthenium tetroxide and conc. hydrochloric acid until the evolution of chlorine has ceased. This requires about two days. Potassium chloride is then added to the strongly acidic soln. of ruthenium trichloride, in small quantities at a time, and crystals of potassium chloroperruthenite are deposited. The salt is washed free from acid by alcohol, and dried by exposure over conc. sulphuric acid. R. Samuel and A. R. R. Despande studied the absorption spectrum of some complex chlorides. G. F. Hüttig discussed the hydrate $K_2RuCl_5.H_2O$. According to S. C. Lind, an aq. soln. of potassium chloroperruthenite changes its colour from red to black owing to hydrolysis. The reaction is represented $K_2RuCl_5+2H_2O=2KCl+2HCl+Ru(OH)_2Cl$. The state of equilibrium, corresponding with the hydrolysis of about two-thirds of the salt to **ruthenium dihydroxychloride,** $Ru(OH)_2Cl$, is not altered by dilution, by

the addition of acid, or by a change of temp., so that the reaction is irreversible and the final state is not that state of equilibrium to which this term is usually applied. The subject was studied by H. Freundlich and A. Paris. The addition of alkali hydroxide to the hydrolyzed soln. was found by S. C. Lind and F. W. Bliss to give an immediate precipitation of hydrated ruthenium sesquioxide.

The potassium chloroperruthenite, K_2RuCl_5, prepared by the addition of potassium chloride to cold, acidified soln. of ruthenium trichloride, was found by A. Miolati and C. C. Tagiuri to furnish reddish-buff, feathery crystals of the *monohydrate,* although the evaporated mother-liquor furnishes crystals of the anhydrous salt. A. Gutbier and co-workers, and R. Charonnat also found that the alkali chloroperruthenites furnish the monohydrates. When crystallized from hot acidified soln., J. L. Howe and L. P. Haynes obtained dark brownish-red, tetragonal octahedra or plates of the anhydrous salt. If the aquo-salt, $K_2Ru(H_2O)Cl_5$—*vide infra*—be dehydrated the resulting potassium chloroperruthenite has somewhat different properties. The ordinary chlororuthenites are called **α-chloroperruthenites,** and those obtained by dehydrating the aquo-salts, **β-chloroperruthenites.** If the potassium chlororuthenate be heated in a current of dry hydrogen chloride at 540° to 560°, S. Aoyama obtained what he regarded as **potassium γ-chloroperruthenite ;** but A. Gutbier and W. Niemann, and J. L. Howe and L. P. Haynes claimed that the γ- and β-forms are the same. J. L. Howe and L. P. Haynes gave the comparison shown in Table I for the α- and

TABLE I.—COMPARISON OF SOME PROPERTIES OF POTASSIUM α- AND β-CHLOROPERRUTHENITES.

	α-K_2RuCl_5	$K_2Ru(H_2O)Cl_5$	β-K_2RuCl_5	K_2RuCl_6
Soln. in water	Dissolves slowly; pale reddish-yellow soln.	Easily soluble ; pale pink soln.	Dissolves readily ; yellow, fluorescent soln.	Rapidly dissolves ; reddish-yellow soln. ; quickly hydrolyzes.
Addition chlorine	No change	Darkens ; dark green pp. in conc. soln. leaving pale yellow soln.	Darkens slightly on standing	No change.
Addition NaOH	Green soln. ; dark pp. on standing	Loses colour ; black pp. on boiling	Blue soln. becoming pale green ; dirty green pp. on boiling	Loses colour ; then dirty green.
Addition H_2S	Colourless, then dark brown pp., and azure-blue liquid	Colourless, then darkens ; black pp. but no blue soln.	Green soln. changes to deep blue which in some days becomes opaque and gives black pp.	Colourless ; purplish-brown pp.

β-forms. The results with the γ-form were the same as for the β-form. The β- and γ-salts when crystallized from aq. soln. both yield the aquo-salt. The soln. at first are yellow, and they become pink after standing for some hours. The yellow soln. becomes blue on adding sodium hydroxide, but not so after standing for some hours. S. C. Lind and F. W. Bliss found that while the α-salt is two-thirds hydrolyzed to $Ru(OH)_2Cl$ in dil. soln., the β-salt is only one-third hydrolyzed under similar conditions to form **ruthenium hydroxydichloride,** $Ru(OH)Cl_2$.

The normal, brown monohydrate—the α-monohydrate—$K_2RuCl_5.H_2O$, is different in some respects from its isomer potassium aquochloroperruthenite—the β-monohydrate—$K_2Ru(H_2O)Cl_5$. These salts were examined by J. L. Howe, and A. Miolati and C. C. Tagiuri. The α-salt forms a deep brownish-red soln.; it gives

up two atoms of chlorine on hydrolysis, but is not changed to chlororuthenate by chlorine. The α-salt is changed into the β-salt by the action of some organic agents—*e.g.*, alcohol, phenol, oxalic acid, but not acetic acid—and by some reducing agents—*e.g.*, stannous chloride. The β-salt gives a rose-red soln.; it gives up one atom of chlorine on hydrolysis; and chlorine converts it into chlororuthenate. The β-monohydrate is, according to J. L. Howe, an aquo-salt in which the water is much more firmly retained than is the case with the α-monohydrate. S. H. C. Briggs assigned to what is here called the β-monohydrate the formula $2K_2RuCl_5.3H_2O$, but J. L. Howe could not confirm this. A. Gutbier and W. Niemann observed no evidence of the existence of a γ-form reported by S. Aoyama.

R. Charonnat argued that the red β-salt, and the brown α-salt, are not isomerides, but differ in respect of the valency of the contained ruthenium. He said that the brown α-salt is not transformed by chlorine into hexachlororuthenate, and it contains less water than corresponds with the monohydrate; the red salt is formed from the brown salt by a reducing agent, it loses a mol. of water between 140° and 180°, and chlorine converts it into the chlororuthenate. The brown α-salt, but not the red β-salt, liberates iodine from potassium iodide and hydrochloric acid. The valency of the red β-salt is determined by its preparation from potassium trioxalatoperruthenite, $K_3[Ru'''(C_2O_4)_3]$. These facts agree with the assumption that the red β-salt is **potassium aquochloroperruthenite,** $K_2[Ru'''(H_2O)Cl_5]$, and that the brown α-salt is **potassium hydroxychlororuthenate,** $K_2[Ru''''(OH)Cl_5]$. J. L. Howe said that (i) the liberation of iodine from potassium iodide by the α- and not by the β-salts is not conclusive; (ii) the fact that the β-salt is formed when the oxalatoperruthenite is treated with hydrochloric acid is in agreement with the formation of the β-salt from the α-salt by oxalic acid; (iii) although the β-salt is formed from the α-salt by reducing agents, it has not been shown that the process is one of reduction. S. H. C. Briggs added that the ruthenium in the α-salt is not likely to be quadrivalent because (i) it was formed directly from the tervalent chloride and potassium chloride, by A. Miolati and C. C. Tagiuri, and by A. Gutbier and co-workers; (ii) a reducing agent is not necessary for the conversion of the α- to the β-salt, since hydrochloric acid will effect the transformation; and (iii) the oxidation of the β-salt with oxygen does not yield the α-salt, but rather a totally different substance, $K_2RuCl_5.K_2RuCl_5(OH)$. H. Remy and A. Lührs also believed that the brown α-salts contain quadrivalent ruthenium, $K_4[Ru_2OCl_{10}]$—*vide supra*, ruthenium tetrachloride.

J. L. Howe, K. Trenkner, and A. Gutbier and K. Trenkner, prepared **rubidium chloroperruthenite,** $Rb_2RuCl_5.H_2O$, by the action of hydrochloric acid on ruthenium tetroxide, and the subsequent addition of rubidium chloride to the soln. The product is a dark brown powder fairly soluble in water and in hydrochloric acid. R. Charonnat doubted the existence of this salt. The analogous **cæsium chloroperruthenite,** $Cs_2RuCl_5.H_2O$, was prepared in the same manner. There is what J. L. Howe supposes to be an isomeride, cæsium chloroaquoperruthenite, $Cs_2Ru(H_2O)Cl_5$—*vide supra*, the potassium salt—obtained by heating a slightly acidic soln. of cæsium chlororuthenate with water and alcohol—*vide supra.* F. Krauss and E. Bruchhaus studied this salt. A. Miolati and C. C. Tagiuri obtained a soln. of **sodium chloroperruthenite,** Na_2RuCl_5, by the action of organic substances on a soln. of sodium chlororuthenate or simply by warming a soln. of sodium chlororuthenate. The brownish-yellow soln. gives a precipitate of potassium chloroperruthenite when treated with potassium chloride; and when boiled with sodium hydrosulphite, a precipitate of $Na_7Ru(SO_3)_5.2H_2O$. V. Ipatéeff studied the action of hydrogen under press.

R. Charonnat prepared **potassium hexachloroperruthenite,** $K_3[RuCl_6].H_2O$, in red crystals; **ammonium hexachloroperruthenite,** $(NH_4)_3[RuCl_6].H_2O$, in red plates; **pyridinium hexachloroperruthenite,** $(C_5H_6N)_3[RuCl_6].H_2O$, as a deep red crystalline powder; and **sodium hexachloroperruthenite,** $Na_3[RuCl_6].12H_2O$,

in red crystals, which are very soluble in water, and melt in their own water of crystallization.

J. L. Howe prepared **potassium chloroaquoperruthenite,** $K_2Ru(H_2O)Cl_5$, by boiling a soln. of potassium chloroperruthenite, acidified with hydrochloric acid, with alcohol, or by boiling a soln. of the hydrated sesquioxide in hydrochloric acid with alcohol. The salt crystallizes in rhombic octahedra, which, according to R. Charonnat, are isomorphous with corresponding salts of tervalent iron, thallium, iridium, and rhodium. According to J. L. Howe, when the aq. soln. is boiled, it becomes greenish-brown, and the soln. is immediately darkened on adding chlorine water or bromine water. The salt is stable up to 140°, and it loses water between 140° and 180°, passing into the anhydrous chloroperruthenite, K_2RuCl_5. S. Aoyama and T. Fukuroi studied the absorption spectrum of soln. of the potassium pentachlororuthenite and its aquo-salt in hydrochloric acid, and obtained definite evidence of the existence of all three salts: potassium α-, β-, and γ-pentachlororuthenites. The chloroaquoperruthenites are isomeric with the monohydrated chlororuthenites. Crystals of the dehydrated potassium aquo-salt are pseudomorphs after the original salt. The aq. soln. of the two salts behave differently; both soln. are hydrolyzed with a corresponding increase in conductivity, but the increase with the chloroperruthenite is slower than it is with the aquo-salt, and whilst the initial values of the two salts are the same, the final value for the aquo-salt is less than it is for the chloroperruthenite—*vide supra* for a discussion on this subject. R. Charonnat said that the crystals of $K_2[Ru(H_2O)Cl_5]$, and those of $K_2[Fe(H_2O)Cl_5]$, are isomorphous. J. L. Howe also prepared **ammonium chloroaquoperruthenite,** $(NH_4)_2Ru(H_2O)Cl_5$, by boiling ammonium chloroperruthenite with dil. acidified alcohol; it crystallizes with difficulty; chlorine converts the salt into the chlororuthenate. J. L. Howe prepared **cæsium chloroaquoperruthenite,** $Cs_2Ru(H_2O)Cl_5$, as a buff-coloured precipitate on adding alcohol to the blue filtrate from electrolytically-reduced soln. of ruthenous trichloride and cæsium chloride. The rose-red prisms are slightly soluble in water, and may be crystallized unchanged from the soln. in hydrochloric acid.

J. L. Howe prepared **potassium nitrosylchloroperruthenite,** $K_2RuCl_5(NO)$, or $2KCl.RuCl_3.NO$, as a precipitate, by the action of conc. soln. of potassium chloride on ruthenium nitrosyl chloride; and by the evaporation of mixed dil. soln. of these two salts. The black, rhombic crystals form a reddish-violet soln. with water, and the aq. soln. was found by S. C. Lind to suffer no change in conductivity in two weeks; ionization occurs in accord with $K_2RuCl_5(NO) \rightleftharpoons 2K^{\cdot} + Ru(NO)Cl_5'$. The salt was also prepared by R. Charonnat. C. Claus thought this salt was a chlororuthenate, but A. Joly showed that it is a nitroso-salt; and he obtained the *dihydrate* in black efflorescent crystals by slow evaporation. J. L. Howe prepared **rubidium nitrosylchloroperruthenite,** $Rb_2Ru(NO)Cl_5$, and its *dihydrate*; also **cæsium nitrosylchloroperruthenite,** $Cs_2Ru(NO)Cl_5$, and its *dihydrate*; and A. Joly, **ammonium nitrosylchloroperruthenite,** $(NH_4)_2Ru(NO)Cl_5$, and its *dihydrate*. R. Charonnat prepared **ruthenium nitrosylhydroxyhydrochloridobisethylenediaminochloride,** $[Ru(NO)(OH.HCl)\,en_2]Cl_2$.

A. Gutbier and F. Krauss prepared **methylammonium chloroperruthenite,** $(CH_3.NH_3)_2RuCl_5$; **dimethylammonium chloroperruthenite,** $\{(CH_3)_2NH_2\}_2RuCl_5$; **trimethylammonium chloroperruthenite,** $\{(CH_3)_3NH\}_2RuCl_5$; **tetramethylammonium chloroperruthenite,** $(CH_3)_4NRuCl_5$; **ethylammonium chloroperruthenite,** $(C_2H_5.NH_3)_2RuCl_5$; **diethylammonium chloroperruthenite,** $\{(C_2H_5)_2NH_2\}_2RuCl_5$; **triethylammonium chloroperruthenite,** $(C_2H_5)_3NH\}_2$-$RuCl_5$; **tetraethylammonium chloroperruthenite,** $\{(C_2H_5)_4N\}_2RuCl_5$; *n*-propylammonium chloroperruthenite, $(C_3H_7.NH_3)_2RuCl_5$; **iso-propylammonium chloroperruthenite,** $(C_3H_7.NH_3)_2RuCl_5$; **dipropylammonium chloroperruthenite,** $\{(C_3H_7)_2NH_2\}_2RuCl_5$; **tripropylammonium chloroperruthenite,** $\{(C_3H_7)_3NH\}_2$-$RuCl_5$; *n*-**butylammonium chloroperruthenite,** $(C_4H_9.NH_3)_2RuCl_5$; **iso-butylammonium chloroperruthenite,** $(C_4H_9.NH_3)_2RuCl_5$; **di-iso-butylammonium**

chloroperruthenite, $\{(C_4H_9)_2NH_2\}_2RuCl_5$; **tri-iso-butylammonium chloroperruthenite,** $\{(C_4H_9)_3NH\}_2RuCl_5$; **guanidinium chloroperruthenite,** $\{NH:C(NH_2)_2\}_2RuCl_5$; **ethylenediammonium chloroperruthenite,** $\{C_2H_4(NH_3)_2\}RuCl_5$; **pyridinium chloroperruthenite,** $(C_5H_6N)_2RuCl_5$; **β-picolinium chloroperruthenite,** $(C_5H_4.CH_3.NH)_2RuCl_5$; **piperidinium chloroperruthenite,** $(C_5H_{10}.NH_2)_2RuCl_5$; and **quinolinium chloroperruthenite,** $(C_9H_7.NH)_2RuCl_5$.

A. Gutbier, and A. Gutbier and F. Krauss prepared **methylammonium heptachloroperruthenite,** $(CH_3NH_3)_4RuCl_7$, or $[RuCl_2(NH_3.CH_3Cl)_4]Cl$; **ethylammonium heptachloroperruthenite,** $(C_3H_7NH_3)_4RuCl_7$; ***n*-propylammonium heptachloroperruthenite,** $(C_3H_7NH_3)_4RuCl_7$; **iso-propylammonium chloroperruthenite,** $(C_3H_7NH_3)_4RuCl_7$; ***n*-butylammonium heptachloroperruthenite,** $(C_4H_9NH_3)_4RuCl_7$; **iso-butylammonium heptachloroperruthenite,** $(C_4H_9NH_3)_4RuCl_7$; **ethylenediammonium heptachloroperruthenite,** $(C_2H_4.N_2H_6)_2RuCl_7$; **propylenediammonium heptachloroperruthenite,** $(C_3H_6.N_2H_6)_2RuCl_7$; and **pyridinium heptachloroperruthenite,** $(C_5H_5.NH)_4RuCl_7$. R. Charonnat prepared **pyridinium hexachloroperruthenite,** $(C_5H_6N)_3[RuCl_6].H_2O$; **pyridinium pentachloropyridinoperruthenite,** $(C_5H_6N)_2[Ru,pyCl_5]$, and **pyridinium tetrachlorobispyridinoperruthenite,** $(C_5H_6N)[Ru,py_2Cl_4]$. The following two compounds with co-ordination numbers of 8 were prepared: **ethylenediamine aquoheptachloroperruthenite,** $\{C_2H_4(NH_2)_2\}[Ru(H_2O)Cl_7]$, in red crystals which are decomposed by water, and lose hydrogen chloride when dried at 100° ; and **ethylenediamine hydroxyheptachloroperruthenite,** $\{C_2H_4(NH_2)_2\}[Ru(OH)Cl_7]$, in brown crystals which are readily reduced by hydrogen. R. Charonnat also prepared numerous derivatives of oxalates and nitrosylchlorides and strychnine, pyridine, etc. F. M. Jäger and H. B. Blumendal noted the rotatory dispersion of some derivatives. R. Charonnat obtained this salt by reducing potassium hydroxypentachlororuthenate with alcohol in the presence of hydrochloric acid.

According to A. Miolati and C. C. Tagiuri, and J. L. Howe, when hydrated ruthenium dioxide is dissolved in hydrochloric acid, the yellow soln. contains **ruthenium tetrachloride,** $RuCl_4$. L. Wöhler and P. Balz could not prepare the anhydrous tetrachloride from chlororuthenic acid, or by chlorinating the trichloride. According to W. R. Crowell and D. M. Yost, if a hydrochloric acid soln. of ruthenium hydroxide is chlorinated, all the ruthenium is converted into the quadrivalent state, and the electrometric titration of the soln. with titanous sulphate, before and after chlorination, shows an end-point when ruthenium is reduced to the tervalent, not the bivalent state. Although ruthenium tetrachloride itself has not been isolated, R. Charonnat prepared **ruthenium dipyridinotetrachloride,** $[Ru,pyCl_4]$; and double salts—**chlororuthenates**—with the alkali metals have been prepared. The salt was also obtained by R. Charonnat, and S. Aoyama. U. Antony obtained **potassium chlororuthenate,** K_2RuCl_6, by adding hydrochloric acid to potassium ruthenate, and U. Antony and A. Lucchesi recommended the following procedure :

A mixture of 6 parts of potassium hydroxide and 1 part of powdered ruthenium is heated to fusion in a silver basin, and potassium chlorate added in small quantities with stirring until the ruthenium is completely dissolved. After heating at a high temp. until all evolution of gas ceases, the excess of chlorate being then decomposed, the cold mass, which is of an orange-red colour, is dissolved in cold water, and very dil. hydrochloric acid added until the soln. gives a decided acidic reaction. When allowed to evaporate at the ordinary temp. in vacuo over quicklime, this liquid gradually deposits the chlororuthenate which is purified by repeated crystallization.

J. L. Howe obtained the same salt by the action of chlorine on a conc. soln. of potassium chloroaquoperruthenite ; and S. Aoyama, by the action of conc. hydrochloric acid on ruthenium tetroxide, and subsequently treating the liquid with potassium chloride as indicated in connection with the ammonium salt. S. Aoyama also prepared it by treating a soln. of hydroxytetrachlororuthenic acid in conc. hydrochloric acid for 5 hrs., at 100°, and evaporating the liquid spontaneously at

ordinary temp., first over sulphuric acid, and then over phosphoric oxide, while a current of chlorine is passing through the liquid the whole time. Hygroscopic, reddish-brown, monoclinic crystals of the *pentahydrate*, $RuCl_4.5H_2O$, are formed. S. Aoyama and T. Fukuroi studied the absorption spectrum of K_2RuCl_6 in hydrochloric acid soln. U. Antony and A. Lucchesi said that the salt forms a reddish-brown, crystalline powder; and J. L. Howe, black octahedra with a greenish sheen. S. Aoyama said that the pentahydrate melts at 25°; loses 2·5 mols. of water at 57°; 4 mols. at 78°; and 4·5 mols. at 100°. The hydrate was studied by G. F. Hüttig. The salt obtained by U. Antony and A. Lucchesi was sparingly soluble in cold water, and insoluble in a soln. of potassium chloride. The salt is soluble in hot water, and it is decomposed in aq. soln. J. L. Howe found the salt to be readily soluble in and to be decomposed by water. A dil. soln. in hydrochloric acid is yellow, and a conc. soln., deep yellowish-red. According to S. Aoyama, the conc. soln. is stable at the ordinary temp., does not liberate iodine from potassium iodide, gives a black precipitate with silver nitrate, and yields crystalline double salts with potassium and ammonium chlorides. The dil. soln. slowly hydrolyzes with the formation of a black, colloidal soln., yields silver chloride on the addition of silver nitrate, liberates iodine from potassium iodide, and first a colloidal, brown soln., then a yellowish-brown precipitate of ruthenium trisulphide is obtained on saturation with hydrogen sulphide. O. W. Gibbs observed that probably complex salts are formed when ruthenium chloride is treated with ammonium molybdate or sodium tungstate.

J. L. Howe observed that **ammonium chlororuthenate,** $(NH_4)_2RuCl_6$, is formed when chlorine is passed into a conc. aq. soln. of the chloroperruthenite. S. Aoyama obtained the ammonium salt, $(NH_4)_2RuCl_6.\frac{1}{2}H_2O$, by the interaction of conc. hydrochloric acid and ruthenium tetroxide, the soln. being heated, saturated with a mixture of chlorine and hydrogen chloride, kept for some hours, and then again saturated with chlorine and hydrogen chloride. The mixture is then cooled in ice and treated with conc. ammonium chloride soln., when the ammonium chlororuthenate separates in pale brown, star-shaped crystals belonging to the cubic system. These crystals dissolve in water to form a brown soln., which on dilution first turns yellow and then deposits a black precipitate owing to hydrolysis. The salt is slowly but completely decomposed by hydrogen sulphide, the whole of the ruthenium being precipitated. The blue colour test for ruthenium is not sensitive in this case. A. Gutbier, H. Zwicker, A. Gutbier and F. Krauss, and A. Gutbier and H. Zwicker obtained some derivatives, thus, **methylammonium chlororuthenate,** $(CH_3.NH_3)_2RuCl_6$, in greenish-brown, hexagonal leaflets; **dimethylammonium chlororuthenate,** $\{(CH_3)_2NH_2\}_2RuCl_6$, in glistening dark needles; **trimethylammonium chlororuthenate,** $\{(CH_3)_3NH\}_2RuCl_6$, in dark green needles; **tetramethylammonium chlororuthenate,** $\{(CH_3)_4N\}_2RuCl_6$; **ethylammonium chlororuthenate,** $(C_2H_5.NH_3)_2RuCl_6$, in glistening, green needles; **diethylammonium chlororuthenate,** $\{(C_2H_5)_2NH_2\}_2RuCl_6$, in glistening, brownish-green needles; **triethylammonium chlororuthenate,** $\{(C_2H_5)_3NH\}_2RuCl_6$, in black plates; **tetraethylammonium chlororuthenate,** $\{(C_2H_5)_4N\}_2RuCl_6$; **propylammonium chlororuthenate,** $(C_3H_7.NH_2)_2RuCl_6$, in glistening, dark green needles; **dipropylammonium chlororuthenate,** $\{(C_3H_7)_2NH_2\}_2RuCl_6$, in dark green needles; **tripropylammonium chlororuthenate,** $\{(C_3H_7)_3NH_3\}_2RuCl_6$; **butylamineammonium chlororuthenate,** $(C_4H_9NH_2)_2RuCl_6$, in glistening dark green leaflets; **di-iso-butylammonium chlororuthenate,** $\{(C_4H_9)_2NH_2\}_2RuCl_6$; **tri-iso-butylammonium chlororuthenate,** $\{(C_4H_9)_3NH\}_2RuCl_6$; **di-iso-amylammonium chlororuthenate,** $\{(C_5H_{11})_2NH_2\}_2RuCl_6$; **ethylenediammonium chlororuthenate,** $(C_2H_4:N_2H_6)_2RuCl_6$, in glistening black needles; **propylenediammonium chlororuthenate,** $(C_3H_6:N_2H_6)_2RuCl_6$, in greenish-black needles; **benzylammonium chlororuthenate,** $(C_6H_5.CH_2.NH_3)_2RuCl_6$, in brown needles; **pyridinium chlororuthenate,** $(C_5H_5NH)_2RuCl_6$, in brown needles; α- and **β-picolinium chlororuthenate,** $\{C_5H_4(CH_3):NH\}_2RuCl_6$, in bronze-coloured plates; **piperidinium**

chlororuthenate, $(C_5H_{10}.NH_2)_2RuCl_6$; and **quinolinium chlororuthenate,** $(C_9H_7.NH)_2RuCl_6$.

J. L. Howe prepared **rubidium chlororuthenate,** Rb_2RuCl_6, as in the case of the potassium salt, and likewise also **cæsium chlororuthenate,** Cs_2RuCl_6, in black, almost opaque, regular octahedra, slightly soluble in water. F. Krauss also prepared this salt. A. Miolati and C. C. Tagiuri observed that when chlorine acts on a mixture of sodium and ruthenium chlorides, and the product of the reaction is lixiviated with water, a dark red liquid supposed to contain **sodium chlororuthenate,** Na_2RuCl_6, is obtained. If the soln. be hot and dilute, or if it be placed in contact with organic substances, it becomes brown, and then contains ruthenium trichloride since potassium chloride precipitates potassium chloroperruthenite. O. W. Gibbs prepared **cobaltic hexamminochlororuthenate,** $[Co(NH_3)_6]_2(RuCl_6)_3$.

According to S. Aoyama, ruthenium tetroxide and hydrogen chloride react to form **tetrachlorodioxyruthenic acid,** $H_2RuO_2Cl_4.3H_2O$, in reddish-brown, needle-shaped, hygroscopic crystals, which dissolve in water to give an acidic soln. When these crystals are treated with conc. aq. hydrochloric acid, chlorine is given off, and a reddish-brown soln. is obtained which contains both hexachlororuthenic acid, H_2RuCl_6, and pentachlororuthenious acid, H_2RuCl_5, whilst the ammonium salts of these two acids are formed if the tetrachloro-oxyruthenic acid be treated with ammonium chloride soln. V. Ipatéeff studied the action of hydrogen under press. H. Remy and A. Lührs said ruthenium tetroxide reacts initially with conc. hydrochloric acid to form ruthenium dioxydichloride, RuO_2Cl_2, which is rapidly reduced further by excess of acid to ruthenium tetrachloride. This compound is unstable in soln., decomposing either into the trichloride or into the hydroxytrichloride. Pure soln. of the latter substance can be prepared readily, and from them the " hydrated pentachlororuthenates " or hydroxypentachlororuthenates. They also said that freshly-prepared soln. of ruthenium tetroxide in conc. hydrochloric acid contain ruthenium tetrachloride, or the corresponding acid as shown by the preparation of the alkali salts. When soln. of the tetrachloride are heated, hydrolysis occurs, and **ruthenium hydroxytrichloride,** $Ru(OH)Cl_3$, is formed. The change proceeds slowly even in soln. saturated with hydrogen chloride. In moderately dil. soln. the process is arrested when one chlorine atom is replaced by hydroxyl and proceeds beyond this stage only in soln. containing much less hydrochloric acid. In addition, the reduction of ruthenium with evolution of chlorine, $RuCl_4=RuCl_3+Cl$, can occur, but, contrary to some observers, they state that this action is hindered rather than accelerated by rise in temp. unless a current of indifferent gas is passed through the soln. If carbon dioxide is passed until chlorine is no longer evolved, a partial reduction to tervalent ruthenium is observed unless the conditions for hydrolysis have been provided before driving out the chlorine. Soln. of ruthenium hydroxytrichloride do not evolve chlorine when treated with carbon dioxide and the valency of the metal does not alter. Soln. of the trichloride prepared by F. Krauss and H. Kükenthal, and H. Gall and G. Lehmann, contain some quadrivalent chloride. The evaporation to a syrupy consistency with conc. hydrochloric acid has little influence on the valency of ruthenium unless repeated very frequently. A more marked effect is produced when the soln. are evaporated to dryness, but, in every case, the process comes to a conclusion when about half of the metal has passed into the tervalent state. Further reduction could not be effected by repeated evaporation to dryness extending over more than a week. It is therefore impossible to obtain the pure trichloride by simply evaporating with hydrochloric acid a product containing large amounts of quadrivalent ruthenium. J. L. Howe prepared **rubidium tetrachlorodioxyruthenate,** $Rb_2RuO_2Cl_4$, or $2RbCl.RuO_2Cl_4$, and also **cæsium tetrachlorodioxyruthenate,** $Cs_2RuO_2Cl_4$, by covering ruthenium tetroxide with water, acidulated with hydrochloric acid, to which rubidium or cæsium chloride has been added. The salts furnish dark purple cubes and rhombic dodecahedra belonging to the cubic system. The salts are soluble in cold hydrochloric acid from which they may be recrystallized

unchanged. Boiling hydrochloric acid forms the chlororuthenate with the evolution of chlorine. The salts are instantly decomposed by water, and the water becomes black. R. Charonnat prepared **methylammonium dihydroxytetrachlororuthenate,** $(CH_3.NH_3)[Ru(OH)_2Cl_4]$, in red crystals, soluble in water.

According to F. Krauss, when the salt corresponding with ammonium ruthenate (*q.v.*) or rather ruthenium dioxydihydroxydiammine is treated with hydrochloric acid, it yields **ruthenium dioxydiaquodichlorodiammine,** $RuO_2(H_2O)_2(NH_3)_2Cl_2$, which is reconverted into the dioxydihydroxydiammine on treatment with aq. ammonia.

As indicated in connection with potassium chloroperruthenite, R. Charonnat assumed that the brown α-salt is **potassium hydroxypentachlororuthenate,** $K_2[Ru(OH)Cl_5)$, where the ruthenium is quadrivalent, whilst the red β-salt is potassium aquopentachloroperruthenite, $K_2[Ru(H_2O)Cl_5)$, with tervalent ruthenium. S. H. C. Briggs found that when a hot acidified soln. of J. L. Howe's potassium aquochloroperruthenite is oxidized by exposure to air, it furnishes a potassium hydroxychlororuthenate, $K_2RuCl_5.K_2RuCl_5(OH)$, which, according to J. L. Howe and L. P. Haynes, is a mixture of anhydrous and ordinary monohydrated α-chloroperruthenite. R. Charonnat prepared the hydroxypentachlororuthenate by the action of hydrochloric acid on ruthenium tetroxide, and hydrolyzing the product. R. Charonnat observed that when this salt is reduced by alcohol in the presence of hydrochloric acid, potassium aquopentachloroperruthenite is formed. A. Joly observed that **ruthenium hydroxyheptamminodichloride,** $2Ru(OH)Cl_2(NH_3)_7.3H_2O$, also called *ruthenium red,* is formed when the finely-divided, anhydrous trichloride is projected in successive small quantities into an aq. soln. of ammonia, sat. at a low temp., and the mixture is heated for some time at 40°. The deep red, conc. soln. deposits brown lamellæ with a metallic lustre by reflected light, and yellow by transmitted light; the soln. is red by transmitted light, and has a violet tinge by reflected light. A soln. of one part of the compound in 10,000 parts of water has an intense red colour, and even 1 part in 5,000,000 parts of water has a distinct rose colour. The dry salt is stable when exposed to light, but its soln. decompose with precipitation of the brown sesquioxide. Decomposition is rapid when the soln. is boiled, and intermediate products are formed either by loss of ammonia or by progressive substitution of the elements of water for chlorine. When conc. hydrochloric acid is added to conc. soln., **ruthenium hydroxyheptamminohydrotrichloride,** $2Ru(OH)Cl_2(NH_3)_7.HCl.3H_2O$, separates as a brown precipitate. The red coloration that appears on boiling an ammoniacal soln. of the nitroso-oxychloride is due to the formation of the ammoniacal hydroxychloride now described, and is not due to the reproduction of the original nitrosochloride by loss of ammonia. When the salt is dissolved in water, it forms a yellow soln., but as the proportion of water is increased, the colour changes to red. A small quantity of ammonia or other alkali changes the colour at once to reddish-violet. By double decomposition with silver nitrate in acid soln., the hydrochloride yields readily crystallizable salts, forming yellow soln. which become red on the addition of a base. The use of ruthenium red for staining tissues, etc., in histology was indicated by L. Mangin, and by A. Nicolle and J. Cantacuzene.

C. Claus obtained **potassium nitrosylchlororuthenate,** $K_2Ru(NO)Cl_5$, and it was studied by A. Joly, and J. L. Howe. The salt is formed by the action of potassium hydroxide and nitrate on ruthenium in a silver crucible. The mass is extracted with water and the soln. treated with hydrochloric acid, until the black precipitate at first formed redissolves. The crystals obtained on evaporating the liquid are purified by recrystallization. The salt can also be obtained by the action of hydrochloric acid on a double nitrite, or by adding potassium nitrite to a hydrochloric acid soln. of the trichloride. H. Dufet observed that the black crystals are rhombic. They are soluble in water, forming a violet-red soln.; the conc. soln. is black and opaque. The soln. is stable, and S. C. Lind observed that its electrical

conductivity does not vary during 3 days. The *dihydrate* obtained by A. Joly is deposited in black crystals by the slow evaporation of the aq. soln. The crystals effloresce in air. The boiling aq. soln. deposits the anhydrous salt. L. Brizard, and C. Claus prepared the complex salt $Ru_2H_2(NO)Cl_3.2HCl.3KCl$. J. L. Howe prepared **cæsium nitrosylchlororuthenate,** $Cs_2Ru(NO)Cl_5$, and also the *dihydrate*; and A. Joly, and H. Dufet, **sodium nitrosylchlororuthenate,** $Na_2Ru(NO)Cl_5.3H_2O$; and a complex $Ru_2H_2(NO)Cl_3.2HCl.3NaCl$; A. Joly, and J. L. Howe prepared **ammonium nitrosylchlororuthenate,** $(NH_4)_2Ru(NO)Cl_5$, and the *dihydrate,* as well as a complex $Ru_2H_2(NO)Cl_3.2HCl.3NH_4Cl$.

A. Joly said that A. Claus' nitrosyl compound can be represented $RuX_2.NO.OH(NH_3)_4$, where X denotes the acidic radicle. There is **ruthenium tetrammino-dichloride,** $RuCl_2(NH_3)_4.3H_2O$; **ruthenium nitrosylhydroxytetramminodichloride,** $RuCl_2(NH_3)_4NO(OH)$; and **ruthenium nitrosylhydroxytetramminochloroplatinite,** $RuCl_2(NH_3)_4NO(OH)PtCl_4$; L. Brizard reported a series of salts illustrated by **ruthenium dihydronitrosylhydroxydichloride,** $Ru_2(NO)H_2(OH)Cl_2$; **ruthenium dihydronitrosyltrihydroxide,** $Ru_2(NO)H_2(OH)_3$; **ruthenium dihydronitrosylhydro-chloride,** $Ru_2(NO)H_2Cl_3.2HCl$; **ruthenium dihydronitrosylhexamminohydro-chloride,** $Ru_2(NO)H_2(NH_3)_6Cl_3.2HCl$, and double salts with ammonium, potassium, and silver chlorides, and with potassium bromide.

H. Gall and G. Lehmann prepared **ruthenium dibromide,** $RuBr_2$, by reducing the tribromide, in absolute alcoholic soln., in the presence of bromoform—*vide supra,* ruthenium dichloride. W. Strecker and M. F. Schurigen, and M. F. Schurigen obtained **ruthenium phosphobromide,** $2RuBr_2.5PBr_3$, by the action of phosphoric pentabromide on spongy ruthenium. A. Joly prepared **ruthenium tribromide,** $RuBr_3$, by the action of hydrobromic acid on ruthenium tetroxide; A. Gutbier and K. Trenkner, by evaporating an aq. soln. of the tetroxide with conc. hydro-bromic acid; and F. Krauss and H. Kükenthal, by heating the trihydroxide in the corresponding hydrogen halide at 100° to 110°. J. L. Howe obtained a reddish-purple soln. of **bromoperruthenous acid,** H_2RuBr_5, by covering rubidium tetroxide with a 50 per cent. soln. of hydrobromic acid. O. Ruff and E. Vidic said that the first stage of action of hydrobromic acid on ruthenium tetroxide involves the formation of *ruthenium tetrabromide* which very quickly decomposes to form the tribromide. Ruthenium tribromide is dark brown, and gives off bromine when heated. It forms with water a bright red soln. which decomposes slowly at ordinary temp., rapidly when heated, and yields a black precipitate. F. Krauss and H. Kükenthal found that the soln. in conc. hydrochloric acid is brown, and after boiling it is red. According to O. Ruff and E. Vidic, hydrogen sulphide forms ruthenium sulphide. The solid bromide absorbs dry ammonia. F. Krauss and H. Kükenthal said that the salt forms a green soln. with aq. ammonia, which becomes wine-red when boiled; the soln. in alcohol is violet; and the dark green soln. in potassium cyanide soln. becomes violet-blue when boiled, to form **ruthenium hemiheptaamminotribromide,** $2RuBr_3.7NH_3$. G. T. Morgan and F. H. Burstall prepared the bromine analogues of ruthenium red (*q.v.*), and derivatives.

According to W. Manchot and co-workers, ruthenium tribromide is converted by carbon monoxide at 185° to 188° and 350 atm. into colourless, crystalline **ruthenium carbonyl bromide,** $RuBr(CO)$, a complex of univalent ruthenium, **ruthenium mono-bromide,** $RuBr$. The carbonyl is slowly decomposed by water, and it reduces ammoniacal silver soln. It evolves carbon monoxide when heated in nitric oxide at 220°, and in carbon monoxide, at 200°, it forms ruthenium, and **ruthenium dicarbonyldibromide,** $RuBr_2(CO)_2$, a complex of **ruthenium dibromide,** $RuBr_2$. A. Joly prepared **ruthenium nitrosyltribromide,** $Ru(NO)Br_3.H_2O$; and L. Brizard, **ruthenium dihydronitrosylhydrobromide,** $Ru_2(NO)H_2Br_3.2HBr$, and the double salt **potassium nitrosylbromoruthenate,** $K_2Ru(NO)Br_5$, as in the case of the corre-sponding chloro-salts; and the complex salt $Ru_2H_2(NO)Br_3.2HBr.3KBr$; and $Ru_2H_2(NO)Cl_3.3KBr$, as well as **ruthenium dihydronitrosylhexamminohydro-bromide,** $Ru_2(NO)H_2(NH_3)_6.Br_3.2HBr$. H. Dufet obtained **potassium nitrosyl-**

bromoperruthenite, $2KBr.RuBr_3.NO$. R. Charonnat prepared **ruthenium nitrosylbromobisethylenediamminobromide,** $[Ru(NO)Br\,en_2]Br_2$. W. Manchot and J. König found that the tribromide with carbon monoxide at 270° to 290° forms ruthenium dicarbonyldibromide; an aq. or alcoholic soln. of the tribromide absorbs carbon monoxide very slowly. Ruthenium tribromide forms double salts with the alkali bromides—the **bromoperruthenites,** which form dark blue soln. with water. The soln. becomes reddish-brown and ultimately reddish-purple when warmed with hydrobromic acid.

J. L. Howe, K. Trenkner, and A. Gutbier and K. Trenkner prepared **potassium bromoperruthenite,** $K_2RuBr_5.H_2O$, by adding potassium bromide to a soln. of ruthenium tetroxide in hydrobromic acid, and evaporating the soln. over sulphuric acid, and by adding potassium chloride to a soln. of bromoperruthenous acid. The brown crystals are decomposed by water. With rubidium bromide in place of potassium chloride there is formed **rubidium bromoperruthenite,** $Rb_2RuBr_5.H_2O$, which crystallizes from dil. hydrobromic acid. Similarly with **cæsium bromoperruthenite,** $Cs_2RuBr_5.H_2O$; and with **ammonium bromoperruthenite,** $(NH_4)_2RuBr_5.H_2O$. By boiling and then evaporating a soln. of potassium bromoperruthenite with alcohol and hydrobromic acid, J. L. Howe prepared brown crystals of **potassium bromoaquoperruthenite,** $K_2Ru(H_2O)Br_5$; and likewise also brownish-black crystals of **rubidium bromoaquoperruthenite,** $Rb_2Ru(H_2O)Br_5$; and **cæsium bromoperruthenite,** Cs_2RuBr_5.

A. Gutbier and co-workers prepared **methylammonium bromoperruthenite,** $(CH_3NH_3)_2RuBr_5$, in acicular crystals; **dimethylammonium bromoperruthenite,** $\{(CH_3)_2NH_2\}_2RuBr_5$; **trimethylammonium bromoperruthenite,** $\{(CH_3)_3NH\}_2RuBr_5$; **tetramethylammonium bromoperruthenite,** $\{(CH_3)_4N\}_2RuBr_5$; **ethylammonium bromoperruthenite,** $(C_2H_5NH_3)_2RuBr_5$; **diethylammonium bromoperruthenite,** $\{(C_2H_5)_2NH_2\}_2RuBr_5$; **triethylammonium bromoperruthenite,** $\{(C_2H_5)_3NH\}_2RuBr_5$; **tetraethylammonium bromoperruthenite,** $\{(C_2H_5)_4N\}_2RuBr_5$; ***n*-propylammonium bromoperruthenite,** $(C_3H_7NH_3)_2RuBr_5$; ***iso*-propylammonium bromoperruthenite,** $(C_3H_7NH_3)_2RuBr_5$; **dipropylammonium bromoperruthenite,** $\{(C_3H_7)_2NH_2\}_2RuBr_5$; ***n*-butylammonium bromoperruthenite,** $(C_4H_9NH_3)_2RuBr_5$; ***iso*-butylammonium bromoperruthenite,** $(C_4H_9NH_3)_2RuBr_5$; ***iso*-amylammonium bromoperruthenite,** $(C_5H_{11}NH_3)_2RuBr_5$; **ethylenediammonium bromoperruthenite,** $(C_2H_4.N_2H_6)RuBr_5$; **propylenediammonium bromoperruthenite,** $(C_3H_6.N_2H_6)RuBr_5$; **pyridinium bromoperruthenite,** $(C_5H_5.NH)_2RuBr_5$; **β-picolinium bromoperruthenite,** $(C_5H_4.CH_3.NH)_2RuBr_5$; and **quinolinium bromoperruthenite,** $C_9H_7.NH)_2RuBr_5$.

Although **ruthenium tetrabromide,** $RuBr_4$, has not been isolated, **bromoruthenates** have been obtained. Thus, J. L. Howe obtained black, octahedral crystals of **potassium bromoruthenate,** K_2RuBr_6, by passing the vapour of bromine through a conc. soln. of the bromoaquoperruthenite at 0°. W. R. Crowell and D. M. Yost observed that if ruthenium chloride be digested with bromine and hydrobromic acid, and evaporated with potassium bromide, there is formed a salt with quadrivalent ruthenium, probably **potassium hydroxypentabromoruthenate.** J. L. Howe observed that the less soluble **rubidium bromoruthenate,** Rb_2RuBr_6, is produced in a similar way, and likewise also with **ammonium bromoruthenate,** $(NH_4)_2RuBr_6$. A. Gutbier and F. Krauss, A. Gutbier, H. Zwicker, and A. Gutbier and H. Zwicker reported **methylammonium bromoruthenate,** $(CH_3.NH_3)_2RuBr_6$, in black, glistening leaflets; **dimethylammonium bromoruthenate,** $\{(CH_3)_2NH_2\}_2RuBr_6$, in bluish-black, felted needles; **trimethylammonium bromoruthenate,** $\{(CH_3)_3NH\}_2RuBr_6$, in bluish-black needles; **ethylammonium bromoruthenate,** $(C_2H_5.NH_3)_2RuBr_6$, in glistening, green needles; **diethylammonium bromoruthenate,** $\{(C_2H_5)_2NH_2\}_2RuBr_6$; **triethylammonium bromoruthenate,** $\{(C_2H_5)_3NH\}_2RuBr_6$, in black needles; **propylammonium bromoruthenate,** $(C_3H_7.NH_3)_2RuBr_6$, in bluish-black, felted needles; **dipropylammonium bromoruthenate,** $\{(C_3H_7)_2NH_3\}_2RuBr_6$, in dark green needles; **butylammonium**

bromoruthenate, $(C_4H_9.NH_2)_6RuBr_6$, in glistening, bluish-black, felted needles; *ido*-**amylammonium bromoruthenate,** $(C_5H_{11}.NH_3)_2RuBr_6$; **ethylenediammonium bromoruthenate,** $(C_2H_4N_2H_3)_2RuBr_6$, in glistening, black needles; **propylenediammonium bromoruthenate,** $(C_3H_6N_2H_2)_6RuBr_6$, in bluish-black needles; **benzylammonium bromoruthenate,** $(C_6H_5.CH_2.NH_3)_2RuBr_6$, in black needles; **pyridinium bromoruthenate,** $(C_5H_5NH)_2RuBr_6$, in bluish-black needles; α-**picolinium bromoruthenate,** $\{C_5H_4(CH_3):NH\}_2RuBr_6$, in bluish-black needles; and **quinolinium bromoruthenate,** $(C_9H_7.NH)_2RuBr_6$.

H. Gall and G. Lehmann obtained indications of the formation of **ruthenium diiodide,** RuI_2, by reducing a soln. of ruthenium triiodide in absolute alcohol saturated with ammonia. W. Manchot and J. König obtained **ruthenium dicarbonyldiiodide,** $RuI_2(CO)_2$. C. Claus prepared **ruthenium triiodide,** RuI_3, by the double decomposition of potassium iodide and ruthenium trichloride in aq. soln. K. Trenkner, A. Gutbier and K. Trenkner, and F. Krauss and H. Kükenthal, obtained it in a similar manner; and O. Ruff and E. Vidic observed that the salt is produced immediately by the action of hydriodic acid on ruthenium tetroxide (*q.v.*). The black, insoluble, amorphous precipitate evolves the whole of its iodine when heated. F. Krauss and H. Kükenthal observed that the black powder is not hygroscopic; it is very sparingly soluble in water, and in hydrochloric acid, it forms a dark brown soln. and a black residue when treated with aq. ammonia. K. Trenkner, and A. Gutbier and K. Trenkner found that it absorbs dry ammonia yielding **ruthenium hemiheptamminotriiodide,** $2RuI_3.7NH_3$; and G. T. Morgan and F. H. Burstall prepared the iodine analogue of ruthenium red (*q.v.*), and derivatives. W. Manchot and J. König obtained **ruthenium dicarbonyl diiodide,** $RuI_2(CO)_2$, by the action of carbon monoxide on the triiodide at 240° to 250°. A. Joly also prepared **ruthenium nitrosyltriiodide,** $Ru(NO)I_3.nH_2O$; and A. Joly, and H. Dufet prepared **potassium nitrosyliodoruthenate,** $K_2Ru(NO)I_5$, as in the case of the corresponding chloro- and bromo-salts. These compounds were studied by W. Manchot and E. Schmid. R. Charonnat prepared **ruthenium nitrosyliodide,** $Ru(NO)I_3$; **ruthenium nitrosylhydroxybisethylenediaminoiodide,** $[Ru(NO)(ON)en_2]I_2$; **ruthenium nitrosylhydroxyethylenediaminoamminoiodide,** $[Ru(NO)(OH)en(NH_3)_2]I_2$; **ruthenium nitrosylhydroxyethylenediaminobispyridinoiodide,** $[Ru(NO)(OH)en(C_5H_5N)_2]I_2$; **ruthenium nitrosylhydroxyhydrochlorobisethylenediamminoiodide,** $[Ru(NO)(OH.HCl)en_2)I_2$; **ruthenium nitrosylbromobisethylenediaminoiodide,** $[Ru(NO)Br\,en_2]I_2$; **ruthenium nitrosyliodobisethylenediaminoiodide,** $[Ru(NO)I\,en_2]I_2$; and **ruthenium nitrosyliodobisethylenediaminobromide,** $[Ru(NO)I\,en_2]Br_2$. F. Krauss and H. Kükenthal found that the triiodide is very sparingly soluble in alcohol, and it forms a brown soln. with potassium cyanide which when boiled becomes violet.

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§ 8. Ruthenium Sulphides and Sulphate

F. Wöhler [1] observed some bright, octahedral crystals in the fine-grained platinum brought from the platinum washings of Borneo, and he called the mineral **laurite**—as a compliment to the wife of a personal friend. The same mineral was observed in the native platinum of Rogue River, Oregon, collected by C. F. Chandler. The analysis led F. Wöhler to employ the formula $12Ru_2S_3.OsS_4$; J. D. Dana, $20RuS_2.Ru_4Os$; C. F. Rammelsberg, Ru_2S_3 ; and after the mineral had been synthesized by H. St. C. Deville and H. Debray, the formula accepted by P. Groth and K. Mieleitner, and others is that of **ruthenium disulphide,** RuS_2, or, if allowance be made for the presence of some osmium—about 3 per cent. $(Ru,Os)S_2$.

C. Claus observed that there is no sign of chemical combination when a mixture

of finely-divided ruthenium and sulphur is heated in an atm. of carbon dioxide. When hydrogen sulphide is passed for a short time through a soln. of the trichloride the precipitate which is formed corresponds with RuS_3, but if the gas be passed through the soln. for several hours, a yellowish-brown sulphide, RuS_2, is formed. L. Wöhler and co-workers studied the subject. U. Antony and A. Lucchesi found that when hydrogen sulphide acts on a soln. of potassium chlororuthenate at 80° to 90°, the black precipitate corresponds with RuS_2. This is considered one of the best ways of preparing the disulphide. The black precipitate obtained by C. Claus by adding ammonium sulphide to a soln. of the oxychloride was considered to be a ruthenium hemitrisulphide, Ru_2S_3, but this has not been confirmed. C. Claus noted that if the dry precipitate be heated in an atm. of carbon dioxide, it becomes incandescent and explodes; and U. Antony and A. Lucchesi observed a violent explosion when the sulphide is heated in air diluted with much nitrogen. E. K. Fritzman studied the oxidation of the sulphide by hypochlorites: W. F. de Jong and A. Hoog said that the precipitate obtained by hydrogen sulphide in soln. of ruthenium chloride which has been heated in an atm. of carbon dioxide consists entirely of RuS_2. The disulphide is also formed by heating ruthenium trichloride with sulphur for 3 days at about 400°. H. St. C. Deville and H. Debray obtained crystals resembling laurite as follows:

A mixture of ruthenium and iron pyrites with a little borax is heated to bright redness during 8 or 10 hrs.; the ruthenium is converted into sulphide, and dissolved by the molten ferrous sulphide. On treating the latter after cooling with hydrochloric acid, a mixture of the two sulphides of ruthenium is left undissolved; the one occurs as a black powder, soluble in nitric acid, with conversion into ruthenium sulphate; the other, crystallized in cubes or regular octahedrons, has the metallic lustre and bluish colour of laurite.

According to F. M. Jäger and J. H. de Boer, ammonium sulphide added to a soln. of a salt of quadrivalent ruthenium at 100°, forms brownish-black ruthenium disulphide and free sulphur.

Laurite occurs in spheroids and small grains, but more usually in small iron-grey octahedra with faces often rounded like the diamond. According to F. Wöhler, the crystals belong to the cubic system; and the (111)-cleavage is distinct. The crystals were described by A. des Cloizeaux, P. Niggli, and V. M. Goldschmidt. W. F. de Jong and A. Hoog, and I. Oftedal said that the X-radiograms correspond with a lattice of the pyrites type; V. M. Goldschmidt, and I. Oftedal calculated for the lattice parameter edge a=5·57 A., and the sp. gr. 6·33 on the assumption that 4 mols. are present in unit cell; and W. F. de Jong and A. Hoog, 6·28. L. Pauling and M. L. Huggins discussed the subject. F. Wöhler found the sp. gr. of laurite to be 6·99, and its hardness 7·5. R. Juza and W. Meyer gave 6·14 to 6·15 for the sp. gr. F. A. Bannister gave a=5·59 A., the shortest distance between the ruthenium and sulphur atoms is 2·35 A. H. St. C. Deville and H. Debray observed that when heated to the softening temp. of a fireclay crucible, ruthenium disulphide is decomposed and metallic ruthenium is formed. R. Juza and W. Meyer measured the isothermal curves of the vap. press. of the sulphur at 1153° and 1185° and obtained the results shown in Fig. 4. This is taken to mean that there is no evidence of the formation of a sulphide lower than RuS_2. The vap. press. of the sulphur, p mm., is

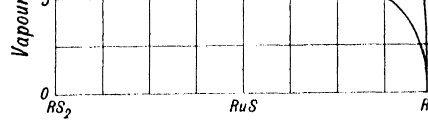

FIG. 4.—Pressure-Concentration Curve of Ruthenium Disulphide.

	1123°	1153°	1184°	1208°
p	2·8	5·4	10·0	15·3

The heat of the reaction is $RuS_2=Ru+S_2=77$ Cals. at 1170°; and the heat of formation at ordinary temp. with solid constituents is $(Ru,2S)=42$ Cals. According to H. St. C. Deville and H. Debray, the mineral is insoluble in all acids and in aqua regia. It is not attacked by fused potassium hydrosulphate. When heated in hydrogen, hydrogen sulphide is formed. It dissolves in a molten mixture of potassium hydroxide and nitrate. V. N. Ivanoff observed no complex formation with thiocarbamide.

According to U. Antony and A. Lucchesi, **ruthenium trisulphide,** RuS_3, is obtained as a yellowish-brown precipitate when hydrogen sulphide is passed into a soln. of potassium ruthenichloride kept at 0°. In the dry state, the sulphide is readily oxidized in the air and becomes heated to incandescence, so that it is necessary to dry it in an atm. of carbon dioxide.

F. M. Jäger and J. H. de Boer observed that when a soln. of a salt of quadrivalent ruthenium is treated with ammonium sulphide, brownish-black disulphide and free sulphur are formed at 100°, but at 0°, greenish-black **ruthenium hexasulphide,** RuS_6, is produced which has the character of an irreversible colloid and with excess of ammonium sulphide gives a green, unstable colloidal soln. At intermediate temp. mixtures of both sulphides and free sulphur are formed. The dark green sulphide and the green colloidal soln. of the hexasulphide (containing positively charged particles) rapidly absorb free oxygen, forming a reddish-violet soln. of the reversible colloid ruthenium pyrosulphide, the particles of which are positively charged. This salt is in turn converted by oxygen (air, nitric acid, permanganate) into ruthenium sulphate and free sulphuric acid. R. Juza and W. Meyer did not succeed in preparing a pure trisulphide by the action of sodium sulphide on a soln. of sodium ruthenate. After extracting the free sulphur with a hot, conc. soln. of sodium sulphide, the products corresponded with $RuS_{2\cdot50}$.

C. Claus observed that when ruthenium sulphide, obtained by treating the chloride with hydrogen sulphide, is digested in nitric acid, there is formed an orange-yellow soln. of **ruthenium sulphate,** $Ru(SO_4)_2$, which, when evaporated to dryness, furnishes a reddish-brown, amorphous mass. U. Antony and A. Lucchesi obtained a red soln. of the sulphate by dissolving barium ruthenate in conc. hydrochloric acid, evaporating the liquid to dryness, extracting the dry mass with water, and adding an excess of dil. sulphuric acid. The concentration of the filtrate furnishes a red liquid but not the crystalline sulphate. A soln. of the sulphate is also formed when ruthenium tetroxide is dissolved in sulphuric acid; and the orange-yellow soln. is evaporated. C. Claus observed that the yellowish-brown, deliquescent solid has a sour, astringent taste, and is readily dissolved by water. On adding alkali lye to the aq. soln., no precipitate is formed at first, but on evaporation, or warming the soln., the hydrated oxide is precipitated. Hydrogen sulphide does not produce the blue reaction obtained with soln. of the chloride. Sulphur dioxide was found by U. Antony and A. Lucchesi to convert it into the dithionate. J. L. Howe and E. A. O'Neal obtained no success in the attempt to prepare *ruthenium* alums. A. Joly prepared **ruthenium nitrosylhydroxytetramminosulphate,** $RuSO_4(NO)OH(NH_3)_4$.

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§ 9. The Ruthenium Ammines

C. Claus [1] described two classes of ammino-compounds, namely, *ruthenous tetramminohydroxide*, $Ru(NH_3)_4(OH)_2$, and *ruthenium diamminohydroxide*, $Ru(NH_3)_2(OH)_2$, but A. Joly showed that these products contained both hydroxyl and nitrosyl groups linked to the ruthenium so that the former were represented by $Ru(NH_3)_4(NO)(OH)X_2$, and the latter by $Ru(NH_3)_2(NO)(OH)_3.H_2O$. They were discussed by H. Schwarz. A. Werner confirmed A. Joly's observation with respect to the presence of the nitrosyl group, and regarded these compounds as derivatives of quadrivalent ruthenium, with the co-ordination number 6. There are a number of groups of the nitrosylammines:

I. *Hydroxynitrosyltetrammines*, $[Ru(NH_3)_4(NO)(OH)]X_2$, and they are represented by (1) hydroxide, $[Ru(NH_3)_4(NO)(OH)](OH)_2$; (2) chloride, $[Ru(NH_3)_4(NO)(HO)]Cl_2$, and its chloroplatinate, $[Ru(NH_3)_4(NO)(OH)]PtCl_6$; (3) hydrochloride, $[Ru(NH_3)_4(NO)(OH)]Cl_2.HCl$; (4) bromide; (5) iodide; (6) sulphate; (7) carbonate; (8) nitrate; and (9) hydronitrate, $[Ru(NH_3)_4(NO)(OH)](NO_3)_2.HNO_3$. These salts were described by C. Claus, A. Joly, H. Dufet, and A. Werner.

II. *Hydroxynitrosylbisethylenediamines*, $[Ru\,en_2(NO)(OH)]X_2$, represented by (1) chloride, $[Ru\,en_2(NO)(OH)]Cl_2$; (2) bromide; (3) iodide; and (4) nitrate. Compounds were also prepared with optically active camphoric acid, camphorsulphonic acid, nitrocamphor, and tartaric acid.

III. *Chloronitrosyltetrammines*, $[Ru(NH_3)_4(NO)Cl]X_2$, represented by (1) chloride, $[Ru(NH_3)_4(NO)Cl]Cl_2$, and its chloroplatinite, $[Ru(NH_3)_4(NO)Cl]PtCl_4$; (2) iodide; and (3) nitrate.

IV. *Bromonitrosyltetrammines*, $[Ru(NH_3)_4(NO)Br]X_2$, represented by (1) bromide; (2) iodide; (3) sulphate; and (4) nitrate.

V. *Nitratonitrosyltetrammines*, $[Ru(NH_3)_4(NO)(NO_3)]X_2$, represented by the nitrate, $[Ru(NH_3)_4(NO)(NO_3)](NO_3)_2$.

VI. *Sulphatonitrosyltetrammines*, $[Ru(NH_3)_4(NO)(SO_4)]_2X_2$, illustrated by the sulphate, $[Ru(NH_3)_4(NO)(SO_4)_2]SO_4$, and the hydrosulphate, $[Ru(NH_3)_4(NO)(SO_4)]_2SO_4.\frac{1}{2}H_2SO_4$.

VII. *Aquonitrosyltetrammines*, $[Ru(NH_3)_4(NO)(H_2O)]X_3$, represented by (1) chloride, $[Ru(NH_3)_4(NO)(H_2O)]Cl_3.H_2O$; (2) bromide; and (3) nitrate.

VIII. *Nitrosylpentachlorides*, $R_2[Ru(OH)Cl_5]$, represented by the salt of (1) potassium, studied by A. Joly, J. L. Howe, and S. C. Lind; (2) rubidium, studied by J. L. Howe; (3) cæsium, studied by J. L. Howe; and (4) ammonium salt, studied by A. Joly. L. Brizard also prepared *potassium nitrosylhydrochloride*, $Ru_2(NO)Cl.3KCl.4HCl$.

IX. *Nitrosylpentabromides*, $R_2[Ru(NO)Br_5]$, represented by (1) potassium and (2) ammonium salts of H. Dufet, and A. Joly.

X. *Nitrosylpentaiodides*, $R_2[Ru(NO)I_5]$, represented by (1) potassium and (2) ammonium salts of H. Dufet, and A. Joly.

XI. *Nitrosyldioxalatopyridinoruthenate*, $[Ru(C_5H_5N)(NO)(C_2O_4)_2]R$, represented by nitrosyldioxalatopyridinoruthenate, $K[Ru(C_5H_5N)(NO)(C_2O_4)_2]$, obtained by R. Charonnat.

XII. *Chloronitrosyloxalatobispyridine*, $[Ru(C_5H_5N)_2(NO)(C_2O_4)Cl]$, obtained by R. Charonnat.

XIII. *Tetrachloronitrosylpyridines*, $[Ru(C_5H_5N)(NO)Cl_4]$, obtained by R. Charonnat.

XIV. *Hydroxydichloronitrosylbispyridine*, $[Ru(C_5H_5N)_2(NO)(OH)Cl_2]$, obtained by R. Charonnat.

XV. *Hydroxytrichloronitrosylbispyridine*, $[Ru(C_5H_5N)_2(NO)Cl_3]$, obtained by R. Charonnat. R. Charonnat also prepared complex salts with quinine, and quinidine in place of pyridine.

A. Joly [2] prepared **ruthenium nitrosylhydroxytetramminocarbonate,** $RuCO_3(NH_3)_4(NO)OH$, by the action of silver carbonate on the chloride.

A. Joly [3] prepared **ruthenium nitrosylhydroxytetramminonitrate,** $Ru(NO_3)_2$-$(NH_3)_4(NO)OH$, by the action of silver nitrate on the carbonate; the compounds were studied by R. Charonnat. G. T. Morgan and F. H. Burstall prepared **ruthenium chloronitratotetramminonitrate,** $[RuCl(NO_3)(NH_3)_4]NO_3.4H_2O$.

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CHAPTER LXX

RHODIUM

§ 1. The Occurrence of Rhodium

THE history of **rhodium** has been indicated in connection with the platinum metals. Rhodium occurs in association with the platinum ores, and osmiridium, and it also occurs in association with gold in the mineral **rhodite,** or *rhodium gold*, found in the auriferous sands of Brazil, and Colombia. According to H. St. C. Deville and H. Debray,[1] and S. Kern, rhodite may contain 34 to 43 per cent. of rhodium. The platinum minerals have up to nearly 5 per cent. of rhodium—average, 1·92 per cent. W. H. Wollaston observed 0·4 per cent. of rhodium in a Peruvian ore. N. Wissotsky, and L. Duparc and M. Tikanowitch reported samples of Russian platinum to contain 0·25 to 1·32 per cent. in that from Tagil; 0·24 to 0·77 per cent. in platinum from the water-shed of the river Iss-Swetli-Bor, and Wéressowy-Ouwal; 0·35 to 0·80 per cent. in that from Kamenouchky, Koswinsky, Kanjakowsky, Omountnaïa, and Daneskin-Kamen; 0·61 to 1·66 per cent. in that from Goussewi-Kamen, Kiedrowka, Barantcha, and Solwa; and 1·82 to 2·07 per cent. in that from Goussewka, Schoumika, and Obleiskaya-Kamenka. I. Koifman reported 0·30 to 0·74 in Russian platinum ores; J. J. Berzelius, G. Osann, and C. Claus, 0·96 to 4·44 per cent. in the platinum from Goroblagodat (Ural); J. J. Berzelius, 0·59 to 1·80 per cent. in that from Tagil; H. St. C. Deville and H. Debray, 0·30 to 2·80 per cent. in some Russian ore; J. J. Berzelius, 3·46 per cent. in platinum from Barbacoas (Colombia); H. St. C. Deville and H. Debray, and L. F. Svanberg, 1·20 to 2·16 per cent. in platinum from Choco (Colombia); A. Kromayer, F. Weil, H. St. C. Deville and H. Debray, and F. A. Genth, 0·65 to 2·45 per cent. in platinum from California; P. Collier, 3·10 per cent. in platinum from Plattsburg (New York); G. C. Hoffmann, 1·70 to 3·10 per cent. in platinum from British Columbia; S. Bleekrode, 0·50 per cent. in a sample from Borneo; H. St. C. Deville and H. Debray, 1·50 to 1·85 per cent. in platinum from Australia; J. C. H. Mingaye, 1·30 per cent. in platinum from New South Wales; S. Kern, 4·60 per cent. in platinum from America; and H. St. C. Deville and H. Debray, 2·65 to 4·10 per cent. in platinum from Spain. H. St. C. Deville and H. Debray, and C. Claus reported in osmiridium from the Urals, 0·50 to 7·70 per cent. of rhodium; 0·63 to 12·30 per cent. in the ore from Colombia; 2·60 per cent. in the ore from California; 2·64 per cent. in the ore from Borneo; and 3·04 per cent. in the ore from Australia; and H. L. Wells reported 0·72 per cent. of rhodium in sperryllite. C. Langer and C. Johnson found 0·39 per cent. Ir, Rh, and Ru in the residue from the mattes of the Sudbury nickel-copper sulphide ores, after extracting the nickel and copper; there were also present 1·85 per cent. of platinum; 1·91, Pd; 0·56, Au; and 15·42, Ag. S. Iimori and J. Yoshimura said that the pink china clay from Tanokami, Japan, contains rhodium or ruthenium as a minor constituent.

The general occurrence of rhodium has been discussed in connection with the platinum metals. F. W. Clarke and H. Washington's[2] estimate for the proportion of rhodium in the igneous rocks of the earth's crust is of the order $n \times 10^{-11}$; and I. and W. Noddack gave $9{\cdot}0 \times 10^{-13}$ for the earth's crust; $5{\cdot}0 \times 10^{-6}$ for meteoric iron; $1{\cdot}0 \times 10^{-6}$ for troilite; and for the atomic distribution, oxygen

unity, $1 \cdot 0 \times 10^{-6}$; later, they gave $2 \cdot 2 \times 10^{-8}$ for the earth's crust, and $1 \cdot 9 \times 10^{-6}$ for meteorites. The subject was also discussed by P. Niggli; F. Bernauer, P. Vinassa, and V. M. Goldschmidt and C. Peters also discussed the occurrence of rhodium in coal. H. A. Rowland classed rhodium amongst the elements present in the solar spectrum; but M. N. Saha, and C. E. St. John considered its occurrence in the sun to be doubtful. H. von Klüber said that twenty of the lines in the solar spectrum have been identified with those of rhodium. H. N. Russell studied the subject.

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§ 2. The Extraction and Preparation of Rhodium

The opening up of the platinum ores is discussed in connection with platinum. W. H. Wollaston [1] treated a soln. of the platinum metals with ammonium chloride to remove the platinum; precipitated the palladium by mercuric cyanide; and evaporated the mixture with sodium chloride. When treated with 84 per cent. alcohol, sodium chlororhodate remains behind whilst the corresponding salts of platinum, iron, and copper, if present, pass into soln. An aq. soln. of the sodium chlororhodate gives a black, flaky precipitate of rhodium when treated with zinc. L. N. Vauquelin removed the platinum by adding ammonium chloride, and the filtrate when evaporated to dryness and taken up with cold water leaves a residue of ammonium chloroiridate and chloroplatinate; the palladium and rhodium are separated by evaporating the soln. nearly to dryness, so that the mass solidifies on cooling. The solid is washed with alcohol, is dissolved in water, or in water acidulated with hydrochloric acid. Any platinum salt present remains undissolved. The rhodium salt passes into soln. The liquid is evaporated to dryness and ignited for rhodium.

J. J. Berzelius precipitated most of the platinum and iridium from the soln. by an excess of a sat. soln. of potassium chloride; the filtrate and washings were then acidified with hydrochloric acid and the noble metals reduced by a plate of zinc or iron; the well-washed precipitate was dissolved in aqua regia, the soln. neutralized with sodium carbonate, and the platinum precipitated by mercuric cyanide. The liquid containing rhodium and copper with small proportions of

platinum, and iridium, together with mercury, was evaporated to dryness to drive off hydrogen cyanide. There are two ways of isolating the rhodium: (1) The powdered residue is digested with alcohol of sp. gr. 0·837 to extract the sodium chloroplatinate, chloroiridate, chlorocuprate, and chloromercurate—the chlororhodate remains as a dark red powder. This is washed with alcohol, and ignited at a high temp., or heated at a lower temp. in hydrogen. Sodium chloride is removed by washing with water. (2) The powdered residue is fused with one and a half times its weight of potassium carbonate, and washed first with water and then with hydrochloric acid to remove potash salts and copper. The residue is fused with five times its weight of potassium hydrosulphate, and the cold mass boiled with water. The process is repeated on any undissolved matters until a fusion with potassium hydrosulphate no longer gives a coloured cake. The rhodium soln. thus obtained are evaporated and ignited with an excess of potassium carbonate. The cold mass when leached with water leaves a residue of rhodium oxide which can be ignited at a high temp., or reduced at a lower temp. in hydrogen to obtain the metal.

H. St. C. Deville and H. Debray precipitated platinum and iridium by the addition of ammonium chloride, and precipitated the noble metals in the filtrate and washings acidulated with hydrochloric acid by means of an iron plate. The residue was fused with a mixture of lead and litharge. The remaining button of lead is well cleaned. It contains metals, less easily oxidized than itself, the more oxidizable metals collect in the slag, etc. The lead is digested with nitric acid when lead, copper, and palladium pass into soln., and the insoluble portion, containing rhodium and other metals, is fused with an excess of barium dioxide, lixiviated with water, and treated with aqua regia. This liberates osmium, which can be recovered by distillation, or the poisonous fumes can be boiled off in a fume-chamber. When the osmium has been all expelled the soln. is treated with sulphuric acid to precipitate the barium, and the filtrate is concentrated by evaporation with nitric acid, mixed with ammonium chloride, and taken to dryness on a water-bath. The residue is well washed with a soln. of ammonium chloride to extract the rhodium. When the washings are no longer rose-pink, the filtrate and washings are evaporated with an excess of nitric acid to destroy the ammonium chloride, and the residual rhodium salt is moistened with a soln. of ammonium sulphide, mixed with sulphur, and heated to redness in a closed crucible. The metallic rhodium which remains can be cleaned by boiling with aqua regia and conc. sulphuric acid. The rhodium can be still further purified by fusing it with zinc at a dull red-heat. The cold product is heated with conc. hydrochloric acid to remove the excess of zinc. There remains a crystalline alloy, $RhZn_2$. This is dissolved in aqua regia, an excess of ammonia is added, and the soln. evaporated to dryness. The resulting rhodium chloropentamminochloride is recrystallized to remove iridium, heated with sulphur as before, and finally heated in an oxyhydrogen flame to volatilize any osmium which may be present.

R. Bunsen separated the platinum and palladium in the usual way, and evaporated the soln. to dryness. The dry residue was fused for 2 to 3 hrs. with 6 to 8 times its weight of zinc, adding some ammonium chloride from time to time. The cold mass has an outer stratum, which is easily broken away, and which contains no platinum metals; the next contains particles of zinc and platinum alloy embedded in basic zinc chloride, and it is porous and not very thick; and the inner mass is a crystalline regulus. The middle portion is washed with water and added to the regulus. The mixture is again fused with about a sixth of the amount of zinc previously employed and some ammonium chloride, granulated by pouring in water, and digested with fuming hydrochloric acid. The platinum metals associated with traces of copper, iron, etc., remain as a black powder. The powder is again digested with hydrochloric acid to remove zinc, iron, copper, and lead—the two latter metals pass into soln. owing to the local currents generated by contact with the platinum metals. The residue—rhodium, ruthenium,

and iridium, with traces of platinum, palladium, lead, copper, iron, and zinc—is thoroughly washed, mixed with 3 or 4 times its weight of anhydrous barium chloride, and heated to a high temp. in a current of chlorine. The cold mass is digested in water, when most of the platinum metals pass into soln. The insoluble portion is reduced with hydrogen, alloyed with zinc, digested with hydrochloric acid, and ruthenium remains. The soln. with most of the platinum metals is treated with sulphuric acid to precipitate the barium. The platinum metals are precipitated from the soln. at 100° by means of hydrogen. The platinum and palladium are precipitated first, then the rhodium, and finally the iridium. The operation is stopped when the liquid has acquired a greenish-yellow colour. The separated metals are treated with aqua regia and the platinum and palladium which dissolve are separated as previously indicated; the traces of rhodium and iridium in the mother-liquor can be removed by boiling with potassium iodide. The precipitated iodides are dissolved in aqua regia, and added to the portion not dissolved by aqua regia. The mixture is reduced in hydrogen gas, treated with barium chloride as before, and, after removing the last traces of platinum and palladium by treatment with soda lye, there remains a mixture of rhodium and iridium. The brownish-red liquid is evaporated with hydrochloric acid, and after filtration mixed with a large excess of sodium hydrosulphite, and allowed to stand for 2 or 3 days in the cold. The precipitate contains rhodium; the soln. when warmed gives a precipitate containing rhodium associated with a small proportion of iridium. The filtrate when concentrated to a small vol. gives two precipitates —a curdy precipitate containing iridium associated with a very small proportion of rhodium, and a crystalline precipitate also containing iridium. These two precipitates can be separated by levigation in water. The mother-liquor was free from the platinum metals.

The complete separation of rhodium from iridium was accomplished by treating the yellow precipitates with conc. sulphuric acid. They were brought in small portions into the acid, heated in a porcelain capsule until all the sulphurous acid has escaped, and then left upon the sand-bath until all the free sulphuric acid had been driven off. Upon boiling the mass with water, all the iridium dissolves as sulphate, with a chrome-green colour; while the rhodium remains behind as a flesh-red double salt of soda and rhodium oxide. The rhodium salt was washed by boiling in aqua regia, and decanted with water. It is insoluble in water, hydrochloric and nitric acids, and in aqua regia.

The first yellow precipitate obtained in the cold by the sodium hydrosulphate, gave, by this treatment, the rhodium quite pure. The second and third precipitates, containing much iridium, gave a very fine rhodium, but still slightly contaminated by iridium. The products, therefore, obtained by this treatment with sulphuric acid (which betray their contamination by iridium by their somewhat brownish colour) were collected for themselves, the rhodium separated by treatment with barium chloride, and the operation repeated. The green soln., containing only iridium, was gradually heated in a porcelain capsule, and, afterwards, upon the sand-bath, to remove the excess of sulphuric acid; and, finally, the capsule and its contents were heated to a high temp. in a fireclay crucible. There was formed thereby sodium iridium sulphate. Upon boiling the mass with water, the last remained as a black, insoluble powder, which was readily washed by decantation.

E. Wichers and co-workers based their process on the formation of a relatively insoluble potassium nitritorhodate, $K_3Rh(NO_2)_6$. They said that the precipitate is accompanied by impurities which are thrown out by hydrolysis in the neutral or slightly alkaline soln. This disadvantage was overcome by forming first the much more soluble sodium nitritorhodate, filtering off impurities precipitated by hydrolysis, and then adding ammonium chloride in order to form the relatively insoluble ammonium nitritorhodate. The latter compound is readily decomposed by hydrochloric acid, yielding a soln. of rhodium chloride. Their process for the purification of rhodium is as follows:

Crude rhodium is best converted to a soluble compound by mixing the metal with about two and one-half times its weight of sodium chloride and heating to about 600° in a current of chlorine. The metal and the salt should be mixed intimately, which may be

done by grinding the two together in a ball-mill. The mixture is placed in boats in an electrically heated tube furnace, or other suitable type of furnace, and heated for 2 to 4 hrs. in a stream of chlorine, the temp. finally being raised to incipient fusion. Minor amounts of certain other platinum-metal compounds may distil out, but can be recovered in the cool portion of the furnace or in a receiving flask containing water. The sintered mass is cooled in the atm. of chlorine and is then dissolved in water. Usually there will be some undissolved residue, the amount depending on a number of factors such as the nature and amount of impurities present, the temperature, and the thoroughness with which the metal was mixed with sodium chloride. The treatment of the undissolved residue is repeated until all or nearly all of the rhodium is in soln.

The soln. is diluted so as to contain about 40 grms. of rhodium per litre. It is filtered from any insoluble residue and heated on the steam-bath. Sodium nitrite is added until the colour changes from deep red to yellow, after which the soln. is boiled for about an hour; 500 to 550 grms. of sodium nitrite should be added for every 100 grms. of rhodium. This results in the conversion of rhodium and other platinum metals to double nitrites, all of which are soluble with the possible exception of a mixed double chloride and nitrite of iridium, $Na_3IrCl_6.Na_3Ir(NO_2)_6$, which is very slightly soluble in water. Most of the base metals present are precipitated as hydroxides or basic salts, but some are converted to soluble double nitrites. If the soln. was too conc., some of the rhodium salt may separate out on cooling. In this case, more water is added to redissolve the salt. The precipitate is filtered from the soln. and reworked for the small amount of precious metals which it may contain.

A small amount of sodium sulphide is added to the cold nitrite soln., which is then set aside overnight. This reagent precipitates the lead as well as some of the palladium, platinum, and iridium present in the soln., but very little of the rhodium. Usually 5 to 10 grms. of sodium sulphide are enough to treat a soln. containing several hundred grams of rhodium. After standing overnight the odour of hydrogen sulphide can usually be detected in the soln. This may be taken as indicating a complete reaction. The sulphides are filtered off and worked up separately for the recovery of the precious metals. The filtrate is heated to boiling so that any remaining sodium sulphide will react to precipitate rhodium sulphide, which is filtered off. The soln. is then treated with an additional 30 to 50 grms. of sodium nitrite for each 100 grms. of rhodium, so as to make sure that all of the rhodium will be in the form of the double nitrite. The soln. is cooled and treated with enough of a sat. soln. of ammonium chloride to form the slightly soluble ammonium nitritorhodate, $(NH_4)_3Rh(NO_2)_6$. This compound is a finely crystalline salt, white when pure, but yellowish if contaminated with other metals of the platinum group. The other metals do not form similar salts which are relatively insoluble. Some iridium salt may be precipitated. Indeed, iridium is the most difficult impurity to eliminate after the lead has been separated by the treatment with sodium sulphide. If the original rhodium material contains much iridium, it is well to effect a preliminary separation of this element by precipitation of ammonium chloroiridate.

In the treatment of the sodium nitritorhodate soln. with ammonium chloride several precautions should be observed. The nitrite soln. is usually slightly alkaline and will therefore liberate ammonia when ammonium chloride is added. For this reason a slightly acidic soln. of ammonium chloride is used. A sat. soln. of ammonium chloride containing 10 ml. of hydrochloric acid (sp. gr. 1·18) per litre is satisfactory. The heat of reaction which occurs when the soln. of ammonium chloride is added causes some loss of nitrite because of the spontaneous decomposition of ammonium nitrite formed by the following reaction: $NaNO_2+NH_4Cl=NaCl+NH_4NO_2$. This excessive loss of nitrite results in incomplete precipitation of the rhodium. For this reason the soln. is cooled in running water, preferably below 18°, during and after the addition of ammonium chloride. The precipitate of the ammonium nitritorhodate is allowed to remain in the soln. for about an hour, after which it is filtered off on a suction funnel and washed with cold water. If the salt remains in the soln. for a longer time, it is quite likely to be contaminated because of the slow precipitation of certain impurities, especially iridium. The filtrate is heated to boiling. After the decomposition of residual ammonium nitrite has ceased, the metals left in the soln. are precipitated with hydrogen sulphide. The precipitate of ammonium nitritorhodate is prepared for the next step in the purification by digesting it with hydrochloric acid on the steam-bath. The acid should be diluted with about four vols. of water to avoid too vigorous a reaction. The soln. of rhodium chloride resulting from this treatment is evaporated to a syrup to drive off the excess of acid, and is then diluted and treated with sodium nitrite as before. The whole procedure may be repeated as many times as necessary to obtain rhodium of the desired degree of purity. Five or six treatments have been found sufficient to produce metal in which only the slightest traces of impurities could be detected spectroscopically.

Progress of purification is followed by examining the metals obtained from the mother-liquors resulting from the precipitation of ammonium rhodium nitrite, and also by examining the precipitate obtained with sodium sulphide. Two or three treatments with sodium sulphide have been found sufficient to eliminate lead. When lead can no longer be found, this step is omitted from the cycle of operations.

The final precipitate of ammonium rhodium nitrite may be dried and kept as a source of pure rhodium, but is not suitable for direct ignition to metal. It is better to convert it to ammonium chlororhodate. This is done by dissolving the salt in hydrochloric acid and adding about 5 per cent. more ammonium chloride than is required to form $(NH_4)_3RhCl_6$. This salt is very soluble in water, but can be precipitated by adding to the soln. one and one-half times its vol. of 95 per cent. alcohol. The salt is filtered off, washed with alcohol, and dried. The residual rhodium can be precipitated from the soln. by hydrogen sulphide. Ammonium chlororhodate may be ignited directly to metal, as in the case of the other similar salts. Unless this is done in hydrogen, the metal will be partly oxidized, but may readily be reduced by ignition and cooling in hydrogen.

R. Gilchrist and co-workers separated rhodium and iridium by making two precipitations with titanous chloride from a hot soln. of the sulphate in dil. sulphuric acid (1 : 19). The titanium is removed from the mixed filtrates by cupferron, and the iridium precipitated hydrolytically as described by L. Moser and H. Graber, and R. Gilchrist. B. G. Karpoff separated iridium and rhodium by first alloying the metal with bismuth. K. Hessner discussed the recovery of rhodium.

Other modifications have been employed—by C. A. Martius, C. Claus, E. Frémy, R. Schneider, M. C. Lea, I. Wada and T. Nakazono, and O. W. Gibbs—based on the attack by chlorine and sodium chloride, or by potassium hydrosulphate. W. Palmer, and S. M. Jörgensen obtained rhodium of a high degree of purity by crystallizing rhodium chloropentamminochloride from a soln. of rhodium chloride and an excess of aq. ammonia. The salt can then be transformed into the nitrate, by heating the salt on the water-bath with nitric acid of sp. gr. 1·40 until no precipitation is obtained when the soln. is diluted and treated with silver nitrate ; on cooling, rectangular crystals of rhodium chloropentamminonitrate separate out. The liquid is added to its own vol. of water and the deposited salt filtered and washed, then air-dried, dissolved in warm water, and added to concentrated hydrochloric acid, when iridium-free rhodium chloropentamminochloride is deposited, from which pure rhodium can be obtained. The salt, however, always contains some nitric acid from which it is freed by treatment, first with 7 per cent. sodium hydroxide soln., then with hydrochloric acid. The chloropentamminochloride can be reduced by heating it in a current of hydrogen, and allowing the metal to cool in a current of carbon dioxide. E. Wichers and co-workers did not get such good results with the chloropentamminochloride process as with the potassium nitritorhodate precipitation. According to E. F. Smith, the electrodeposition of rhodium from soln. of acid phosphate is rapid and complete when a current of 0·18 amp. is employed. The deposit is generally black, compact, and adherent. The subject was studied by A. Joly and E. Leidié, and J. Langness.

R. Bunsen observed that finely-divided rhodium, iridium, etc., " possesses the property, upon being gently heated, of exploding weakly, and, when highly heated, with violence, the explosion being accompanied with the evolution of light ; thereby neither hydrogen, nor chlorine, nor nitrogen, nor aqueous vapour are given off ; and, as these are the only elements which it is possible that the metallic powder could have taken up, it must be assumed these metals are, by our treatment, converted into an allotropic condition, and that, upon heating, they return, with more or less energy, to their original condition." The **explosive rhodium** was found by E. Cohen and T. Strengers to lose its explosive character if kept at 100° to 200° for several days, and if prepared in the entire absence of air, it is not explosive. Consequently, they concluded that the explosiveness is due to the union of occluded hydrogen and oxygen to form water and not to an inherent change in the metal itself. This hypothesis is supported by measurements of the amount of heat developed by the explosion. W. H. Swanger found that zirconia crucibles sometimes soften at the temp. attained by molten rhodium ; and they found thoria crucibles were most suitable. They were made by the process of C. O. Fairchild and M. F. Peters. According to W. H. Swanger, as soon as the rhodium melts in the oxyhydrogen flame it begins to spit, small beads of metal

are thrown off very rapidly, and when the melt freezes large excrescences form on the surface. This is presumably due to the evolution of gases which have been absorbed from the flame by the molten metal. By sufficiently reducing the flow of oxygen to the melting torch, this spitting of rhodium can be avoided to a considerable extent and the metal made to freeze with a fairly smooth surface. Molten rhodium in an open crucible in the induction furnace spits badly, and if the furnace current is shut off suddenly so that the metal freezes rapidly, large blisters will grow out from the surface. By proper manipulation of the furnace current the metal can be frozen slowly so that a minimum of blistering occurs, and forgeable ingots are obtained.

The black precipitate of indefinite composition obtained by reducing soln. of rhodium salts with alcohol and potash lye, or with aq. ammonia and ammonium formate, etc., is called **rhodium black.** C. F. Schönbein,[2] and F. Hoppe-Seyler inferred that rhodium black is a mixture of rhodium with its oxide and hydride all in an exceedingly fine state of subdivision. G. R. Levi and R. Haardt studied the structure of the powder. T. Wilm, and H. St. C. Deville and H. Debray observed that rhodium black dissolves in aqua regia, and also in the presence of air, in hydrochloric and conc. sulphuric acids. Precipitated rhodium was found by A. Sieverts and E. Jurisch to furnish a considerable amount of gas—a mixture of carbon dioxide, oxygen, hydrogen, and water—when it is heated in vacuo. A. Gutbier and O. Maisch observed that when heated to 400° to 500° it forms **rhodium sponge** like spongy platinum. W. H. Swanger, and E. Wichers and co-workers prepared rhodium sponges as follows:

Finely-divided commercial or crude rhodium was heated with sodium chloride in an atmosphere of chlorine gas, to a temp. of about 600°. The partially fused mass of sodium rhodium chloride thus obtained was dissolved in water. This soln. was then boiled with an excess of sodium nitrite, which converted the rhodium to the soluble sodium rhodium nitrite. A small amount of sodium sulphide was then added to remove lead as sulphide. Some of the platinum and palladium present was also precipitated, but not much of the rhodium. After filtration, a sat. soln. of ammonium chloride was added to precipitate ammonium rhodium nitrite, $(NH_4)_3Rh(NO_2)_6$. This salt was easily decomposed by hydrochloric acid, yielding a soln. of rhodium chloride. The foregoing process was then repeated as many times as necessary to produce a final product of the desired degree of purity. As ammonium rhodium nitrite is not a suitable salt for reduction to sponge by ignition, it was converted to ammonium rhodium chloride. This salt was ignited in air, and the somewhat oxidized sponge thus obtained was reduced in hydrogen.

Rhodium black is a powerful catalytic agent. Its catalytic properties were studied by I. I. Tschukoff and co-workers, and A. A. Pollitt. According to G. Bredig and T. Blackadder, the presence of sulphur compounds favours its catalytic activity, and the active rhodium black can be prepared by reducing rhodium sesqui-sulphide with formic acid, or by the electrolytic deposition of rhodium black from a soln. of rhodium in 60 per cent. sulphuric acid, by a current of 0·02 amp. at 180°. Inactive rhodium black becomes active after it has been allowed to absorb oxygen for some time. M. Faraday obtained **rhodium films** by reducing the chloride by phosphorus; but not by hydrogen; and S. G. S. Dicker, by the thermal decomposition of the carbonyl.

G. Kernot and F. Arena [3] prepared a soln. of **colloidal rhodium** by sparking rhodium electrodes submerged in ice-cold water using a current of 2 amps. and 110 volts—**3.** 23, 10. The soln. is reddish-brown and is very unstable. A. Gutbier and co-workers prepared colloidal rhodium by reducing a soln. of a rhodium salt with hydrazine hydrate; and A. Lottermoser, by the action of formaldehyde and potassium hydrocarbonate; and A. Gutbier and E. Leutheusser, by titanous chloride. The presence of some impurities may prevent the formation of the hydrosol, which is very unstable. The addition of a protective colloid, say a 1 per cent. soln. of gum arabic, renders the soln. so stable that it can be concentrated in vacuo over sulphuric acid to form a dark brown solid containing 99·4 per cent. of rhodium, and which forms a hydrosol when treated with water. A. Gutbier and

E. Leutheusser said that the colloidal particles are negatively charged. C. Paal and C. Amberger, and C. Zenghelis and B. Papaconstantinou, used sodium protalbate or lysalbate as protective colloids. The colloidal soln. is coagulated by barium sulphate or animal charcoal. J. Donau observed that the colloid colours a borax bead brown; and A. Lancien and M. Pivoteau, the optical dispersion. According to A. Lancein, the soln. prepared by G. Kernot and F. Arena, containing 0·002 grm. of metal per litre, is toxic towards pathogenic organisms, but is without poisonous action on fish, frogs, and dogs, unless employed in very large doses. When rendered isotonic to blood by means of sodium chloride, and stable by the addition of a trace of sodium glycocholate, it was found to have a very beneficial effect in cases of pneumonia, typhoid, peritonitis, enteritis, post-operative septicæmia, and in tuberculosis during febrile periods. The injections were painless, and in fever reduced the temperature to normal. The patient's urine showed an increase in chlorine and uric acid, but a marked diminution in urobilin and in scatole and indole derivatives. Leucocytosis was increased. V. N. Ivanoff obtained a colloid analogous to purple of Cassius by boiling soln. of rhodium salts with stannous chloride.

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§ 3. The Physical Properties of Rhodium

Rhodium obtained by reducing its salts in hydrogen is a grey powder, but the **colour** of the metal which has been fused is white resembling that of aluminium, but is less brilliant than silver. M. Faraday [1] observed that thin films of rhodium in transmitted light vary from brown to grey. L. Holborn and co-workers observed that rhodium foil after being heated to redness acquires a fine-grained, crystalline structure, and the different crystal-faces show different tints. H. Rössler observed that when cupelled with lead and silver, a button is left with a grey coating of rhodium, and when the silver is removed by acid, the rhodium remains as an aggregate of **crystals** consisting of microscopic, six-sided plates, arranged as ladder- or star-shaped aggregates. Crystal aggregates were also obtained by the analogous treatment of alloys with gold, and with bismuth ; in the case of rhodium bismuthide, some octahedral forms are produced. According to A. W. Hull, the **X-radiograms** indicate that rhodium has a face-centred, cubic lattice with side a=3·820 A. ; and the distance between the nearest atoms is 2·700 A. W. H. Swanger gave a=3·77 A. ; and R. W. Drier and H. L. Walker, a=3·799 A. ; T. Barth and G. Lunde, a=3·795 A. E. A. Owen and E. L. Yates, and E. A. Owen and J. Iball gave a=3·7954 A., and calculated that the distance of closest approach of the atoms is 2·684 A. The subject was discussed by R. W. G. Wyckoff, V. I. Iveronova, and A. E. van Arkel. E. A. Owen and E. L. Yates studied the distortion of the lattice by occluded gas. F. M. Jäger and co-workers observed that the X-radiograms of rhodium change in the neighbourhood of 1200°, corresponding with a transition point as a result of **dynamic allotropism,** and this makes the transition point rather indefinite. Both forms exist at ordinary temp., but the proportion of the α-form decreases, and that of the β-form increases with rise of temp. until, at 1000°, only the β-form is present. The α-form has a face-centred cubic lattice, with a=9·211 A., and the β-form also has a face-centred cubic lattice with a=3·79 A. The sp. gr. of the α-form is smaller than is that of the β-form. There is no perceptible heat effect on the transition from the α- to the β-form. These observations agree with the sp. ht. data ; the temp. coeff. of the electrical resistance ; the change in the photochemical effect and thermionic emission observed by H. E. Dixon to alter between 1100° and 1200° ; and the change in the surface radiation observed by C. E. Mendenhall and L. R. Ingersoll. A. Schulze discussed the transition temp.

H. St. C. Deville and H. Debray found the **specific gravity** of the cast, unworked metal to be 12·1. W. H. Wollaston, and R. Hare had previously found 11·0, and J. Cloud, 11·2 for, presumably, metal of a lower degree of purity. F. Mylius and R. Dietz gave 12·6 for cast and hammered rhodium with 1·6 per cent. of other platinum metals. E. Grüneisen gave 12·23 for the metal of a high degree of purity ; L. Holborn and co-workers, 12·44 ; W. H. Swanger, 12·4 ; and T. K. Rose gave 12·222 at 0°/4° for hammered rhodium sponge and 12·472 for compact metal which had been fused in the oxyhydrogen flame. The best representative value is 12·2. A. W. Hull calculated 12·18 from the X-radiogram data. V. M. Goldschmidt calculated 1·342 A. for the **atomic radius.** E. H. Westling, J. C. Slater, G. Hägg, and W. Biltz and K. Meisel studied the packing density, and the atomic radius. I. R. Rydberg gave 4·0 for the **hardness** of the metal on Mohs' scale. C. A. Edwards gave 156 for Brinell's hardness ; and F E. Carter gave for cast rhodium the Brinell's hardness (12·8 kgrms.), 139 ; and W. H. Swanger, 101 ; and a scleroscope hardness of 10. The subject was discussed by C. Johnson. The metal which has been cast is ductile and malleable at a red-heat, but the

metal which has been agglomerated by compression at a high temp. does not work so readily. According to W. H. Swanger, rhodium wire produced by swagging at 800° or over was not ductile at room temp. It could not be straightened out from a sharp bend without fracturing, nor reduced in diameter by cold-drawing. The fracture appeared coarsely crystalline. The end of a piece of such wire could be flattened on an anvil to half its thickness by one sharp blow with a hammer, but fractured when the same thing was attempted with several light blows. E. Grüneisen found the **elastic modulus** to be 32,500 kgrms. per sq. mm. at 17·5° to 19°; and by another method, 28,000 kgrms. per sq. mm. at 16·9° to 17·8°. A. Mallock gave 1·18 for the ratio of Young's modulus at −273°, and at 0°, E. Widder gave $E=E_{20}\{1-0{\cdot}0005128(\theta-20)\}$. C. Schäfer found the **torsion modulus** to be increased 3·69 per cent. for 100° rise of temp. P. W. Bridgman gave for the **compressibility** of rhodium at 30°, $3{\cdot}72\times10^{-7}$, and at a press. p, $dv/v=-0{\cdot}0_6372p+0{\cdot}0_{11}267p^2$; and at 75°, $dv/v=-0{\cdot}0_6381p+0{\cdot}0_{11}267p^2$. L. H. Adams gave $0{\cdot}38\times10^{-6}$ megabars.

H. Fizeau gave $0{\cdot}0_5850$ at 20°, and $0{\cdot}0_5850$ at 40°, and $0{\cdot}0_5858$ at 50°, for the coeff. of **linear expansion,** α. W. H. Swanger observed for the average coeff., α, per degree, between 20° and

	50°	100°	200°	300°	400°	500°
$\alpha\times10^6$ . . .	8·1	8·3	8·5	8·9	9·3	9·6

F. E. Carter gave $0{\cdot}0_584$ at 20°, and $0{\cdot}0_585$ at 40°. H. Holzmann gave $0{\cdot}0_57628+0{\cdot}0_8457(\theta-20)$. S. Valentiner and J. Wallot gave

	−192° to −162°	−162° to −112°	−112° to −75°	−75° to −56°	−56° to −38°	−38° to −14°	−14° to 0·5°	0·5° to 6°	6° to 21°
$\delta\times10^6$.	4·85	6·34	7·46	7·61	7·70	7·82	8·40	7·96	8·76

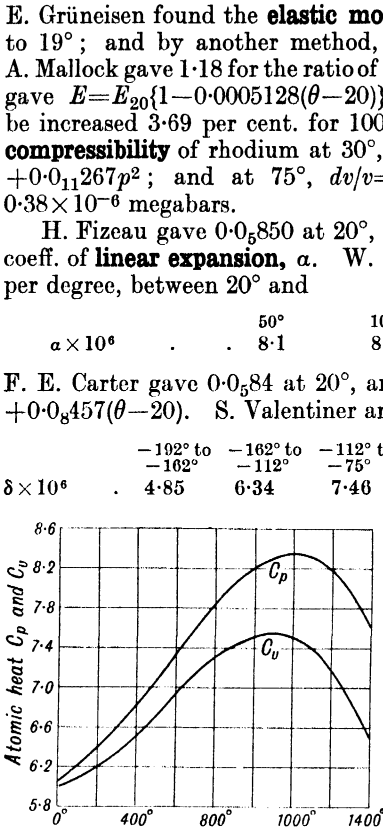

FIG. 1.—The Atomic Heats of Rhodium.

T. Barratt and R. M. Winter found the **thermal conductivity** to be 0·210 cal. per cm. per degree per second at 17°, and 0·192 at 100°; and E. Grüneisen and E. Goens gave 2·15 and 23·8 watts per cm. per degree, at −190° and −252°, respectively. H. V. Regnault found the **specific heat** of rhodium to be 0·0580 between 10° and 97°; and J. Dewar, 0·0134 between −253° and −196°. According to F. M. Jäger and co-workers, the sp. ht. curve rises to a maximum near 1204°, or rather between 1200° and 1470°, as represented by the atomic heat curves, C_p and C_v, in Fig. 1. The following is a selection from their values for the true sp. hts., c_p and c_v, and the at. hts., C_p and C_v:

	0°	100°	300°	500°	700°	900°	1100°	1300°
c_p .	0·05893	0·06026	0·06415	0·06899	0·07393	0·07814	0·08074	0·08092
c_v .	0·05793	0·06013	0·06393	0·06866	0·07348	0·07755	0·08001	0·08008
C_p	6·064	6·201	6·601	7·099	7·607	8·041	8·308	8·327
C_v	5·961	6·063	6·362	6·742	7·125	7·429	7·559	7·422

The results are plotted in Fig. 1. $C_p=0{\cdot}05893+0{\cdot}0_41066\theta+0{\cdot}0_727744\theta^2-0{\cdot}0_{10}17642\theta^3$, up to 1300°. The expression has a maximum at 1204°; and the sp. ht. can be represented by $C_p=0{\cdot}054008+0{\cdot}0_4584608\theta-0{\cdot}0_7869873\theta^2+0{\cdot}0_{10}78256\theta^3-0{\cdot}0_{13}244072\theta^4$ up to 1604°, and this has a maximum at 1470°. The second expression does not fit the observed data so well as the first one at temp. up to 400°. These facts agree with the assumption that there is an allotropic change in the metal between 1100° and 1200°. H. Holzmann found the sp. ht. to be $0{\cdot}060467+0{\cdot}000018303\theta$. E. H. Dixon showed that the sp. ht. at low temp. is not uniquely reproducible on a cooling curve, so that it is assumed that

the metal exhibits dynamic allotropism—*vide supra*. According to F. M. Jäger, the **atomic heats** for C_p and C_v both exceed the value $3R$ cals. at 0°, and rise up to about 8·354 and 7·53 Cals. respectively at 1200°. G. N. Lewis and co-workers gave 7·6 for the **entropy** of rhodium at 25°. A. H. Stuart discussed the relation between the sp. ht. and the elastic constants.

J. Stodart and M. Faraday observed that rhodium fuses imperfectly in the forge-fire; J. Cloud, that it fuses in the oxyhydrogen blowpipe flame to form a steel-grey, hard, brittle button of sp. gr. 11·2; and E. D. Clarke, that rhodium oxide and chloride in the oxyhydrogen blowpipe flame, both yield a malleable, silvery button, and that combustion proceeds at the same time accompanied by a green light, and a volatilization of the metal. J. Cloud, and R. Hare observed that rhodium fuses more readily than platinum; but the impure metal must have been employed. J. L. Byers discussed the behaviour of the metal on cupellation.

H. von Wartenberg observed that with metals of a high degree of purity, if the **melting point** of platinum is 1745°, that of rhodium is 1940°; J. S. Acken gave 1966°. W. F. Roeser and H. T. Wensel gave 1966° for the f.p.—gold, 1063°. L. Holborn and co-workers gave 1946°; W. F. Roeser and co-workers, 1966°; W. H. Swanger, 1985°; O. Feussner and L. Müller, 1970°; W. Guertler and M. Pirini, 1960°; F. E. Carter, 1950°; L. D. Morris and S. R. Scholes, 1966°; and C. E. Mendenhall and L. R. Ingersoll gave 1907° (with Pt, 1745°) for the m.p., and 2500° for the **boiling point** of rhodium—F. E. Carter also gave 2500°. W. R. Mott gave 1950° for the m.p., and calculated 3700° for the b.p. W. Crookes observed that rhodium is half as volatile as platinum at 1300° (*q.v.*); rhodium suffered no perceptible loss during 10 hrs. heating at 900°, and at 1300°,

Time	4	8	12	16	20	24	30 hrs.
Loss .	0·021	0·034	0·049	0·067	0·085	0·107	0·131 per cent.

L. Wöhler and W. Müller found that rhodium is not volatile in air at 1150°. J. H. T. Roberts showed that the rate of loss of weight of rhodium, like that with platinum and iridium, is practically zero when oxygen is absent, and when oxygen is present, the rate of loss of weight diminishes with a diminution in the press. of oxygen. Hence, as in the case of platinum (*q.v.*), the phenomenon is connected with the formation and decomposition of a volatile oxide. G. K. Burgess and co-workers found that when alloyed with platinum, the metal is stiffer and, unlike the case with iridium, the volatility at all temp. above 900° is reduced. F. E. Carter said that appreciable volatilization occurs at 1000°. H. Moissan observed that when heated in the electric arc furnace, rhodium furnishes a blue vapour and distils to furnish spherules consisting of microscopic crystals. H. St. C. Deville and H. Debray, and W. H. Swanger noted that when the molten metal solidifies, it exhibits the phenomenon of spitting—*vide supra*. C. E. Mendenhall and L. R. Ingersoll found that the molten metal may be supercooled as much as 370°—there is a flash due to liberation of heat at the moment of solidification. A. D. van Riemsdijk observed no flashing on cupellation. J. W. Richards estimated the latent **heat of fusion** to be 52 cals. per gram, or 5·1 kilojoules per gram atom.

F. M. Jäger and E. Rosenbohm could detect no appreciable heat effect in the transformation of α-rhodium into β-rhodium. E. D. Eastman, and G. N. Lewis and co-workers calculated 7·49 to 7·60 Cals. for the **entropy** of rhodium at 25°; E. D. Eastman, by different methods, calculated 7·6 to 8·0 cals. at 25°. The internal energy and entropy were studied by R. D. Kleeman, K. K. Kelley, and W. Herz. M. Rabinovitsch studied the glow on heating the finely-divided metal.

W. W. Coblentz [2] found the percentage **reflecting power** of rhodium for light of wave-length, λ in $\mu\mu$, to be:

λ .	500	800	1000	2000	3000	4000	5000	7000	9000
R .	76	81	84	91	92	92·5	93	93·5	94·5

W. W. Coblentz and R. Stair found that the ultra-violet reflecting power of

rhodium increases from 30 per cent. at 260$m\mu$ to 45 per cent. at 365 $m\mu$. Observations were also made by W. H. Swanger. A. de Gramont studied the reflecting power of thin films. H. von Wartenberg observed the **index of refraction,** the absorption coeff., and the percentage reflecting power to be, respectively, 1·54, 4·67, and 78·3 for $\lambda=579\mu\mu$; and 1·81, 5·31, and 79·7 for $\lambda=660\mu\mu$. The **emissivity** is 0·29 at 0·55μ and 0·65μ for the solid, and 0·30 at 0·65μ for the liquid. L. V. Whitney, and F. Henning studied the subject. C. E. Mendenhall and L. R. Ingersoll observed a reversible change in the **radiation** from rhodium at 1050°. F. Henning, F. Henning and W. Heuse, and G. R. Greenslade studied the thermal radiation from rhodium.

Some of the early observations on the spectrum of rhodium were made on impure metal, and those of M. McClean are considered to be of this class. E. Demarçay reported that a line spectrum is obtained by sparking soln. of rhodium salts. The most intense lines of the **spark spectrum** observed by F. Exner and E. Haschek, were 2910·30, 3396·99, 3502·71, 3528·19, 3658·11, 3692·51, 3701·10, 3799·45, 3822·41, 3856·65, 3959·02, and 4375·01. Observations on the spark spectrum were also made by W. E. Adeney, G. Kail, J. M. Eder and E. Valenta, and A. G. Shenstone and J. J. Livingood. E. O. Hulbert, L. H. G. Clark and E. Cohen, and W. F. Meggers studied the under-water spark spectrum. The most intense lines observed by F. Exner and E. Haschek in the **arc spectrum** of rhodium are: 3280·68, 3283·71, 3323·24, 3396·95, 3435·03, 3462·19, 3470·82, 3474·95, 3502·67, 3507·48, 3528·18, 3596·32, 3597·31, 3658·15, 3692·51, 3701·07, 3799·46, 3959·00, 4139·06, 4135·45, 4211·26, 4375·00, 5354·60, 5599·68, and 5983·84. J. Formanek gave for the most intense lines in the visible spectrum, 5984 in the orange-yellow; 5687, 5609, 5600, 5257, 5255, and 5237 in the green; and 4375 in the indigo-blue —Fig. 2. The arc spectrum was also examined by H. A. Rowland, F. Exner and

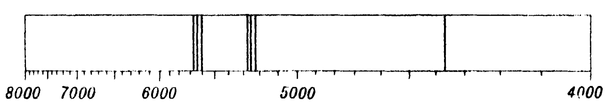

FIG. 2.—Spectrum of Rhodium.

E. Haschek, H. Kayser, L. A. Sommer, W. F. Meggers, A. Hagenbach and H. Konen, and J. M. Eder and E. Valenta. W. Gerlach and co-workers studied the spectrometric determination of rhodium.

The **ultra-violet spectrum** was observed by A. Miethe and B. Seegart, G. Kail, F. Exner and E. Haschek. W. von Bolton observed the spectrum of the **cathodic light** emitted by rhodium electrodes with strong currents. W. J. Humphreys measured the displacement of the lines by pressure; and J. E. Purvis, and L. A. Sommer, the effect of a strong *magnetic field*—the **Zeeman effect.** H. Schüler and H. Gollnow studied the spectroscopic detection of rhodium; and C. P. Snyder, L. A. Sommer, W. F. Meggers and C. C. Kiess, C. C. Kiess and O. Laporte, and O. Laporte, the **series spectra** or the structure of the spectrum or the regularities in the orientation of the lines.

J. Formanek said that conc., brownish-yellow soln. of rhodium chloride exhibit an **absorption spectrum** in all regions but the red and yellow; with dil. soln., there is a weak band in the violet at 4900. There is no characteristic absorption spectra with soln. containing tincture of alkanna; if a neutral soln. of the chloride be treated with tincture of alkanna, the reddish-violet soln. soon becomes bluish-violet, and there is a weak band about 4920. If 2 or 3 drops of aq. ammonia be added, the liquid becomes turbid, and the suspended precipitate shows an absorption band about 6730 which can be utilized for the identification of rhodium. R. Samuel and co-workers studied the absorption spectra of soln. of the salts.

The *K*-series of the **X-ray spectrum** was found by S. K. Allison,[3] M. de Broglie, F. C. and L. P. Chalklin, D. Coster, W. Ehrenberg and H. Mark, G. B. Deodhar, F. Euger, F. C. Hoyt, M. Hulubei and co-workers, O. Laporte, A. Leide,

F. K. Richtmyer and S. Kaufman, P. A. Ross, M. Siegbahn, M. Siegbahn and E. Friman, A. Sommerfeld, E. C. Unnewehr, and J. H. Williams to exhibit lines corresponding with $\alpha_1\alpha$=0·612023, $\alpha_2\alpha^1$=0·616371, $\beta_1\beta$=0·544491, $\beta_2\gamma$=0·533937, and β_3=0·545093. Lines in the L-series were reported by M. Siegbahn, A. Leide, O. Laporte, A. Sommerfeld, F. R. Hirsch and F. K. Richtmyer, J. Zahradnicek, G. D. van Dyke and G. A. Lindsay, E. Friman, and A. Jönsson at $\alpha_1\alpha$=4·58778, $\alpha_2\alpha^1$=4·59556, $\alpha_3\alpha^{11}$=4·572, $l\epsilon$=5·2070, $\eta\eta$=4·9112, L_{I}=3·6208, L_{II}=3·9315, L_{III}=4·1184, $\beta_1\beta$=4·36400, $\beta_2\gamma$=4·1221, $\beta_3\psi$=4·4767, $\beta_4\psi$=4·5126, $\beta_6\nu$=4·2301, $\gamma_1\delta$=3·9357, $\gamma_{2-3}\chi$=3·6770, $\gamma_5\kappa$=4·0352, β_{11}=0·0488, β_{12}=4·0725, and γ_7=3·8968. Observations were also made by P. A. Ross, O. Laporte, A. Jönsson, F. R. Hirsch and F. K. Richtmyer, F. K. and R. D. Richtmyer, and M. J. Druyvesteyn. G. Hagen studied the **Compton effect**; S. Björck, and D. Coster and F. P. Mulder, the X-ray levels; K. Grosskurth, the absorption of X-rays; Y. F. Cheng, the polarization; and E. Fermi and co-workers, **artificial radioactivity.**

O. Laporte[4] studied the **screening constants.** According to E. H. Dixon, when a ribbon of rhodium is subjected to heat treatment at 950° to 1450° in vacuo for 1050 hrs., the long-wave limit shifted from 2530 A. to 3150 A. and back to 2509 A. The photoelectric current increased about 130 per cent. for the temp. range 25° to 950° with a sudden increase at 240°. There is an irregularity in the thermionic current curve at 1100°. L. R. L. Barnes, and H. B. Wahlin studied the emission of positive ions by the hot metal; and F. C. and L. P. Chalklin, the emission of X-rays; J. Chadwick and M. Goldhaber, the photonuclear effect when bombarded with γ-rays; L. Artsimovitsch and co-workers, the capture of slow neutrons by rhodium; K. A. Hofmann and co-workers, F. H. Neuman and H. J. Walke, and E. Amaldi and co-workers, studied the artificial radioactivity; P. B. Moon and J. R. Tillman, the induced radioactivity due to a bombardment with fast neutrons; G. L. Locher, and E. H. Dixon, the **photoelectric effect;** B. B. Ray and D. P. R. Chaudhuri discussed the **ionization potential** of rhodium; and N. Piltschikoff, the **Moser rays.**

W. Broniewsky,[5] and L. Hackspill and W. Broniewsky found the effect of temp. on the **electrical resistance,** R, of rhodium to be 0·70 at −186°; 3·09 at −78·3°; 4·70 at 0°; and 6·60 at 100°. W. H. Swanger gave for the resistance of a 1-mm. wire annealed over 1200°, 4·93 microhms at 20°; and F. E. Carter, 5·11 microhms at 0°. W. Jäger and H. Diesselhorst found the sp. gr. conductivity at 18° to be $16·6\times10^4$ at 18°, and the temp. coeff. of the resistance is 0·00421 between 0° and 100°. W. H. Swanger gave for the temp. coeff. of the resistance between 0° and 100°, 0·00436. L. Holborn, and L. Holborn and A. Day gave for the mean temp. coeff. of the resistance per degree at

	−135°	−39°	50°	150°	250°	350°	450°
R .	0·004367	0·004362	0·004428	0·004599	0·004800	0·005078	0·005278

The subject was studied by E. Grüneisen, A. Schulze, J. T. MacGregor-Morris and R. P. Hunt. W. Meissner and co-workers, and J. O. Linde studied the superconductivity of rhodium at low temp.; E. Grüneisen and E. Goens, the application of Wiedeman-Franz's rule; and F. Simon, and A. T. Waterman, the theory of conductivity. G. Braunsfurth studied the conductivity of thin films; F. M. Jäger and E. Rosenbohm observed that the curve showing the electrical resistance of rhodium as a function of temp. is slightly concave towards the temp. axis between 600° and 1000°; but above 1000°, it becomes slightly convex towards the temp. axis. P. W. Bridgman found the fractional change of resistance, R, with variations of press., p, to be $dR/R=-0·0_51738p+0·0_{10}97p$ at 30°, and at 65°, $dR/R=-0·0_51776p+0·0_9101p^2$. L. Hackspill and W. Broniewsky's value for the temp. coeff. of the resistance is 0·00404, and P. W. Bridgman's, 0·00309. The press. coeff. at 0°, −78·4°, and −182·9°, and 7000 kgrms. per sq. cm., were, respectively, $-0·0_5164$, $-0·0_5142$, $-0·0_5136$. G. Nordström discussed rhodium

for resistance wires in electric furnaces. R. H. Atkinson studied the electrolytic transfer of rhodium using fused alkali chlorides as electrolyte.

L. Holborn and A. Day found the **thermoelectric force** of a *platinum* and rhodium thermocouple with the cold junction at 0°, to be E millivolts, at .

	−185°	−80°	100°	300°	500°	700°	900°	1100°	1300°	1500°
E .	−0·24	−0·31	0·64	2·58	5·12	8·19	11·80	15·88	20·34	25·00

The — symbol means that the current flows through the cold junction to the rhodium. W. H. Swanger gave for the thermoelectric force of rhodium, E millivolts, against purified platinum with the cold junction at 0°,

	0°	100°	200°	400°	600°	800°	1000°	1200°
E . .	0	0·70	1·61	3·92	6·77	10·16	14·05	18·42

F. M. Jäger and E. Rosenbohm found that the increase in the thermoelectric force of the platinum-rhodium thermocouple is continuous, and exhibits no sign of a change due to a transition from one allotropic form to another. L. Hackspill and W. Broniewsky expressed the thermoelectric force of the *copper* and rhodium couple by $dE/d\theta=2·17+0·0005\theta$ millivolts at $\theta°$ between −80° and 100°. J. Monheim studied the rhodium-copper couple.

A. Joly and E. Leidie [6] studied the **electrodeposition of rhodium,** and observed that soln. of rhodium trichloride, or of its complex salts with sodium, ammonium, or potassium chloride, slightly acidified, and containing not more than 4 grms. of metal per litre, furnish coherent deposits of rhodium when electrolyzed at 50° to 60° with a current of 0·5 amp. at the start, and finishing with 0·1 amp. at ordinary temp. The deposition is slow from strongly acidified soln. of the sulphate. The presence of 20 per cent. nitric acid prevents the decomposition of the metal; and with 10 per cent. nitric acid, the deposition is very slow. No rhodium separates at the cathode with soln. containing oxalic acid, but there is a dark green peroxide deposited on the anode. H. Anderssen, R. H. Atkinson and A. R. Raper, L. Cinamon, C. G. Fink and G. C. Lambros, P. Haas, C. W. Keitel and H. E. Zschiegner, J. Langness, O. Macchia, J. Milinaire, I. I. Tschukoff, and A. Wogrinz studied the electrodeposition of rhodium. C. W. Keitel prepared a bath from a 10 per cent. soln. of ammonium sulphate or nitrate with 5 per cent. of free ammonia, and 2 per cent. of rhodium diamminonitrite, replenishing the ammonia and nitrite from time to time. The bath is worked at 95°, with 2·2 volts. H. E. Zschiegner boiled rhodium chloride soln. with sodium nitrite until the liquid was colourless or yellow, and then added an excess of ammonia. A. Simek found that drops of molten tellurium dioxide on hot rhodium do not move as when on platinum. G. Grube and E. Kesting measured the current densities and potentials of soln. of sodium chlororhodate, rhodium trichloride, phosphate, oxalate, perchlorate, sulphate, and fluosilicate. The results with acidified soln. of the sodium chlororhodate are summarized in Fig. 3. They also investigated the influence of the acidity of the soln., and temp. on the deposition of the metal, and they found that even at relatively low current

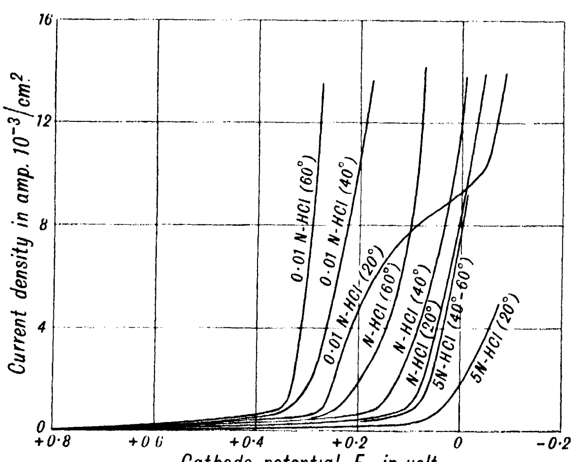

FIG. 3.—Potential-Current Density Curves of Sodium Chlororhodate.

densities, the separation of the metal occurs with the evolution of hydrogen. A. Thiel and W. Hammerschmidt studied the over-voltage of hydrogen. S. Koidzumi examined the anodic behaviour of rhodium in alkaline soln. J. A. V. Butler and G. Drever found that when electrodes of rhodium are anodically polarized in acidic or alkaline soln., an adsorbed layer of oxygen is formed prior to the establishment of the oxygen over-voltage, and there is a slow formation of oxides of a peroxidic character which are reduced cathodically at a more positive potential than the adsorbed oxygen ; J. A. V. Butler and co-workers, the oxidation potential ; and I. Slendyk and P. Herasymenko, the separation of hydrogen from rhodium cathodes.

M. Faraday [7] regarded rhodium as diamagnetic. M. Owen found the **magnetic susceptibility** of rhodium to be $1{\cdot}08\times10^{-6}$ mass unit, and the value increases with a rise of temp. Observations were also made by K. Honda, who gave $1{\cdot}1\times10^{-6}$ mass unit, and W. Finke, who gave $12{\cdot}58\times10^{-6}$ mass unit. B. Cabrera and A. Dupérier gave $Rh^{\cdots}=45{\cdot}5\times10^{-6}$ c.g.s. unit. M. Faraday gave $1{\cdot}1\times10^{-6}$ mass unit. A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility increases with temp. up to 427°. F. H. Loring studied the subject ; and K. Honda and Y. Shimizu, the effect of cold work.

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§ 4. The Chemical Properties of Rhodium

A. Gutbier and O. Maisch [1] observed that rhodium sponge absorbs only traces of **hydrogen ;** and A. Sieverts and E. Jurisch observed that when precipitated rhodium black is heated in vacuo, it evolves a relatively large vol. of mixed gases —hydrogen, carbon dioxide, and oxygen—but after this treatment, the metal does not occlude appreciable quantities of hydrogen or carbon dioxide between 420° and 1020°. F. Hoppe-Seyler regarded rhodium black as a mixture of metal and *rhodium hydride*; and C. F. Schönbein, as a mixture of metal and oxide. I. I. Tschukoff also supposed a hydride is formed. According to A. Gutbier and O. Maisch, the deep black form of rhodium black, A, Fig. 4, absorbs more hydrogen than any other form. The maximum absorption is 180 vols. at 19° for the greyish-black form, C, Fig. 4 ; 165 vols. at about 40° for the slightly greyish-black form ; and 206 vols. at about 0° for the deep black form, A, Fig. 4. Variety A was obtained by reducing sodium chlororhodate in ammoniacal soln. ; C, from faintly acidic soln. ; and B, from neutral soln. The absorption of hydrogen by rhodium

is about the same order of magnitude as it is with platinum. The subject was studied by D. P. Smith, E. Müller and K. Schwabe, and T. Wilm. C. Zenghelis and B. Papaconstantinou observed that the colloidal soln. absorbs hydrogen to the extent of 2510 to 2960 times the vol. of rhodium. E. Müller and K. Schwabe observed that of the hydrogen taken up by reduced rhodium, 100 per cent. is irreversibly absorbed (or chemically combined). H. Remy and H. Gönnington, L. Quennessen, and F. C. Phillips observed that rhodium black accelerates the union of hydrogen and oxygen; and T. Wilm, that the powdered metal with occluded hydrogen becomes hot when exposed to air owing to the oxidation of the hydrogen—*vide supra,* explosive platinum. L. Quennessen showed that rhodium does not absorb hydrogen to anything like the extent reported by T. Wilm. Rhodium heated in a current of hydrogen absorbs a little of the gas, and, on exposure to air, the metal so treated gives rise to a small quantity of moisture, but no moisture is produced if, before the air is admitted, a current of dry cold carbon dioxide is passed over rhodium which has been heated in hydrogen. Further, rhodium previously heated in hydrogen evolves none of this gas when subsequently heated under reduced press.

A. Sieverts and E. Jurisch observed **oxygen** amongst the gases which can be extracted by heating rhodium black in oxygen—*vide supra.* At ordinary temp., **air** and oxygen have no action on rhodium, but J. J. Berzelius observed that the

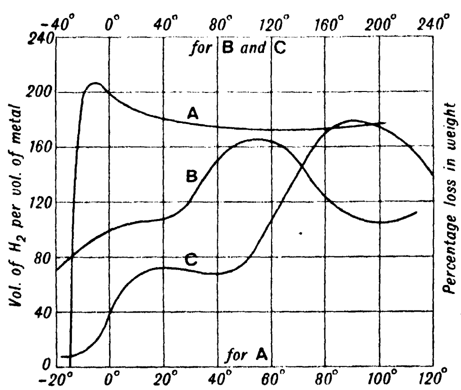

FIG. 4.—The Adsorption of Hydrogen by Rhodium Black.

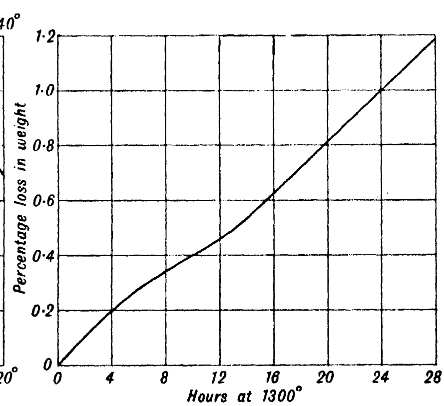

FIG. 5.—Losses in Weight when Rhodium is Heated in Air at 1300°.

metal is oxidized when it is heated in air, and wrongly assumed that the monoxide is formed. A. Gutbier and co-workers showed that when rhodium is heated in air or oxygen between 600° and 1000°, the end-product is the sesquioxide, Rh_2O_3, and that the rate of oxidation increases with the temp. Thus, at

	600°	700°	800°	1000°
Velocity . .	1	30	70	80 units

above 1150°, the oxide is decomposed and rhodium is formed. F. E. Carter said that finely-divided rhodium begins to oxidize to black rhodic oxide at 600°, and that this oxide decomposes into the metal and oxygen at 1150°. L. Holborn and co-workers showed that the metal acquires a bluish tarnish by heat-tinting which is due to oxidation; and that the spluttering or volatilization of rhodium when heated in oxidizing gases to 1610° to 1670° is connected with this phenomenon. W. Crookes observed no decrease in weight at 900° during 8 hrs., but the percentage losses in weight by heating the metal for up to 30 hrs. at 1300° are indicated in Fig. 5. L. Wöhler and W. Müller said that rhodium is not volatile in air at 1150°. F. C. Phillips placed the platinum metals in the order of decreasing catalytic activity: Os, Pd, Pt, Ru, Ir, Rh, and Au in promoting the oxidation of hydrogen. C. Sandonnini and A. Quaglia, and H. Remy and co-workers studied the subject.

K. A. Hofmann, and K. A. Hofmann and O. Schneider found that the catalytic activity of the platinum metals in oxidizing hydrogen in the presence of a soln. of sodium chlorate decreases in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag. C. F. Schönbein observed that rhodium black transforms **ozone** into oxygen. F. Hoppe-Seyler, and G. Kernot and F. Arena found that the catalytic activity of rhodium black towards **hydrogen dioxide** is accelerated by potassium persulphate or percarbonate owing to the formation of a highly oxygenated product more easily decomposed than hydrogen dioxide; potassium perchlorate, perchloric acid, and ammonium persulphate retard the catalysis. The reaction was studied by C. Zenghelis and B. Papaconstantinou. I. I. Shukoff and co-workers, and G. R. Levi studied the subject. Hydrogen dioxide is also decomposed by colloidal rhodium. H. St. C. Deville and H. Debray observed that the metal is oxidized when heated with **barium dioxide.** E. Leidie and L. Quennessen found that rhodium forms an insoluble product when fused with **sodium dioxide.**

O. Ruff observed that rhodium is scarcely attacked by **fluorine** at a red-heat, although J. J. Berzelius observed that with **chlorine,** finely-divided rhodium forms a chloride. A. Gutbier and A. Hüttlinger found that rhodium begins to react with chlorine at 250°, forming the trichloride. L. Wöhler and W. Müller said the reaction occurs between 300° and 968°; rhodium mono- and dichlorides are formed between 948° and 968°. O. Ruff and H. Krug observed that **chlorine trifluoride** attacks the metal with incandescence. C. F. Schönbein, and E. Demarçay noted that rhodium black decomposes chlorine water, and soln. of **hypochlorites,** with the evolution of oxygen. W. H. Wollaston observed that rhodium scarcely dissolves in any acid, but T. Wilm, and H. St. C. Deville and H. Debray found that rhodium black dissolves in **hydrochloric acid** in the presence of air. A. M. Vasileff, and C. Matignon observed that a mixture of hydrochloric acid and air slowly attacks rhodium at 150°. A. Gutbier and A. Hüttlinger found that **bromine** reacts with rhodium at 250°, forming a variable product—possibly partly dissociated tribromide. W. Engelhardt found that **iodine** has no action on the colloid.

J. J. Berzelius observed that rhodium when heated in **sulphur** vapour unites with incandescence, forming a sulphide which decomposes at a high temp. A. Sieverts and E. Jurisch said that **sulphur dioxide** does not dissolve in the metal; and L. Duparc and co-workers studied the activity of the catalyst in the oxidation of sulphur dioxide. S. F. Schemtschuschny found that it dissolves in hot, concentrated **sulphuric** acid; and L. Duparc and co-workers, and P. Wenger and C. Urfer noted the oxidation of sulphur dioxide with rhodium black as catalyst. G. R. Levi and M. Faldini found that the presence of rhodium in a platinum catalyst decreases the yield in the oxidation of sulphur dioxide, owing, said S. Pastorello, to the formation of a rhodium oxide. E. Tiede and R. Piwonka studied the **alumina** rhodium phosphor. Sulphuric acid has no action on rhodium, but H. St. C. Deville and H. Debray, and T. Wilm found that when rhodium black is treated with conc. **sulphuric acid** some metal is dissolved. S. F. Schemtschuschny said that hot, conc. sulphuric acid, with mechanical stirring, dissolves rhodium. W. H. Wollaston said that rhodium is not attacked by **aqua regia,** but T. Wilm, and H. St. C. Deville and H. Debray noted that rhodium black is in part dissolved by aqua regia; and W. H. Wollaston found that some rhodium is dissolved by aqua regia when it is alloyed with copper, lead, bismuth, or platinum, but not with silver or gold; but H. Rössler found that rhodium is dissolved from gold alloys with only 1 per cent. of rhodium. C. Zenghelis and B. Papaconstantinou observed that colloidal rhodium in alkaline soln. forms ammonia from a mixture of hydrogen and **nitrogen;** and L. Duparc and co-workers, I. E. Adaduroff and B. Schenkel studied the oxidation of **ammonia** in the presence of rhodium; **nitrous oxide** is reduced by hydrogen in the presence of rhodium black; and similarly with **nitric oxide.** The reduction of these two oxides was also studied by L. Duparc and co-workers. W. Strecker and M. F. Schurigin, and M. F. Schurigin could not

prepare phosphochlorides or phosphobromides by the action of **phosphorus pentachloride** or **phosphorus pentabromide** on spongy rhodium. N. W. Fischer showed that rhodium dissolves in fused **phosphoric acid.** W. H. Wollaston observed that rhodium readily alloys with **arsenic,** and also with **bismuth.** E. J. Rode studied the alloys of rhodium and **bismuth**; and H. Rössler noted the direct formation of **rhodium bismuthide,** $RhBi_4$. E. J. Rode studied these alloys. H. Moissan found that when rhodium is melted in the presence of **carbon,** about 7 per cent. is dissolved, and rejected as graphite on cooling. H. Wölbling studied the adsorption of rhodium by activated carbon. A. Sieverts and E. Jurisch said that **carbon monoxide** does not dissolve in rhodium; but C. Zenghelis and B. Papaconstantinou observed that colloidal rhodium absorbs carbon monoxide to the extent of 346 times the vol. of rhodium at 12° to 14°, and 1820 times that vol. at 60°. L. Duparc and co-workers, and F. Fischer and co-workers studied activity of the platinum metals as catalysts in the reduction of carbon monoxide to methane. K. A. Hofmann and O. Schneider found that the catalytic activity of the platinum metals in oxidizing carbon monoxide in the presence of a soln. of sodium chlorate decreases in the order Os, Rh, Au, Pt, Ru, Pd, Ir, Ag. B. Schenkel observed that rhodium black acts catalytically on carbon monoxide or **carbon dioxide,** mixed with hydrogen, and methane is formed. L. Duparc and co-workers also studied the reduction of carbon dioxide with rhodium as catalyst. A. Sieverts and E. Jurisch noted that carbon dioxide is present amongst the gases occluded by rhodium black—*vide supra.* The decomposition of **hydrocarbons** in presence of the rhodium catalyst was studied by T. Wilm, and by F. Mylius and C. Hüttner. According to T. Wilm, the action of coal gas on rhodium is quite different from that of palladium, for under the same circumstances not the slightest deposition of carbon takes place on the sides of the crucible or bulb-tube, as is the case with palladium, but it appears to enter into a loose combination with the rhodium, which is largely increased in vol., and assumes an appearance like tea-leaves, or the chromic oxide obtained by the ignition of ammonium chromate. On admitting air to the tube the contents begin to glow, but do not suffer any diminution in vol.; when this has ceased no further combustion of carbon could be observed on passing in a current of air or oxygen. Only after cooling in oxygen and then passing in hydrogen does the glowing recommence, but still without producing any alteration in the vol. of the contents of the tube. The vol. left after the above treatment is equal to three or four times that of the original metal, and is free from carbon. The composition of the mass left after the action of the coal-gas approximates to RhC. F. Mylius and C. Hüttner found that at 100° rhodium takes up sulphur from **carbon disulphide.** According to H. St. C. Deville and H. Debray, rhodium black oxidizes **alcohol** in alkaline soln. to form acetate and hydrogen; and H. St. C. Deville and H. Debray, and E. Müller and K. Sponsel found that it decomposes **formic acid** at ordinary temp. into carbon dioxide and hydrogen. The reaction was studied by C. N. Hinshelwood and B. Topley, P. Pikos, G. Bredig and T. Blackadder, M. Berthelot, N. D. Zelinsky and N. Glinka, and P. Sabatier and A. Mailhe. G. F. Hüttig and E. Weissberger studied the catalytic decomposition of **methyl alcohol**; E. Müller and K. Schwabe studied the catalytic action of rhodium in the oxidation of ethyl alcohol; E. Müller and co-workers, P. Pikos, V. Haas, and T. Blackadder, **formic acid**; L. Tschugaeff, the decomposition of **formaldehyde**; and N. D. Zelinsky and M. B. T. Pollak, the hydrogenation of **benzene.**

W. H. Wollaston found that rhodium can be alloyed with some of the **metals.** Thus, P. G. Ehrhardt observed that a **lithium-rhodium alloy** is harder than rhodium alone. A **copper-rhodium alloy** with 75 per cent. of copper dissolves completely in aqua regia. O. E. Zujagintseff and B. K. Brunovsky observed the presence of rhodium cupride, RhCu, with a transition point of 1015°, and a cubic face-centred lattice; there may also be a rhodium tritacupride, Rh_3Cu. J. J. Berzelius, and W. H. Wollaston prepared **silver-rhodium alloys** which were completely dissolved by aqua regia. H. Rössler said that rhodium

does not alloy with silver, and when rhodium is added to molten silver, it floats on the surface and on cooling is recovered in the amorphous condition. R. W. Drier and H. L. Walker could detect no evidence of the solubility of silver in rhodium. W. Truthe studied the behaviour of the alloy on cupellation. W. H. Wollaston observed malleable **gold-rhodium alloys** with gold (1 : 4 to 1 : 6). The rhodium is not dissolved when the alloy is digested with aqua regia. H. Rössler said that a **rhodium auride** is probably formed, and that an alloy containing 1 per cent. of rhodium is completely soluble in aqua regia; a molten metal with 10 per cent. of rhodium furnishes on cooling feathery crystals of rhodium, and alloys still richer in rhodium give the amorphous metal. R. W. Drier and H. L. Walker observed that the alloys contain two solid soln. The gold lattice contracted a maximum of 0·011 A. by alloying with rhodium, and this is taken to represent a solubility of 4·1 at. per cent. of rhodium in gold. Likewise the edge of unit cell of rhodium expanded a maximum of 0·003 A., showing that the solubility of gold in rhodium is near 1·5 at. per cent. W. Truthe studied the behaviour of the alloy on cupellation. J. O. Linde studied the atomic resistance. A. M. de Rio found that some analyses of gold ores, of sp. gr. 15·5 to 16·8, in the auriferous sands of Colombia, and Brazil, showed the presence of 34 to 43 per cent. of rhodium, and was hence called *rhodiumgold*. M. Adam called the mineral **rhodite.** C. F. de Landero described the Mexican gold-rhodium ores.

H. St. C. Deville and H. Debray, and H. Debray found that rhodium dissolves in molten zinc at a dull red-heat, and that when the zinc-rhodium alloy is treated with hydrochloric acid to remove the excess of zinc, H. Debray observed that there remains a crystalline powder of **rhodium dizincide,** $RhZn_2$. A. J. Bradley, U. Dehlinger, and W. E. Schmid discussed the X-radiograms of rhodium zincide, Rh_5Zn_{21}. Rhodium also alloys with molten tin, and when the excess of tin is removed by hydrochloric acid from the **tin-rhodium alloy,** there remains **rhodium tristannide,** $RhSn_3$. W. H. Wollaston observed that a **lead-rhodium alloy** with 75 per cent. of lead is completely soluble in aqua regia. W. C. Roberts-Austen observed that rhodium diffused in lead at 550° at the rate of 3·035 grms. per sq. cm. per day, or $3·15\times10^{-1}$ grm. per sec. H. Debray found that alloys with 2 or 3 per cent. of lead are attacked by dil. nitric acid, and then leave a crystalline residue of **rhodium diplumbide,** $RhPb_2$. A. Schulze studied the thermoelectric properties of **rhodium-rhenium alloys**; and F. Beck, the etching of the alloys. J. Stodart and M. Faraday prepared **iron-rhodium alloys,** and found that the 1 : 1-alloy of iron or rather steel has a sp. gr. 9·176, and does not tarnish in air, so that a polished surface can be employed as a metal-mirror; a 1 : 50 to 100 alloy is hard and moderately tough and requires a temp. 39° higher than that required for tempering ordinary steel. Some metallurgical, and mechanical, and physical properties of these alloys were determined by R. A. Hadfield. N. Agéeff and M. Zamotorin studied the diffusion of rhodium in steel; J. W. Greig and co-workers, the action of iron oxides on rhodium; and F. Wever, the effect of rhodium on the transition points of iron. H. Remy and H. Gönnington studied the catalytic effect of the iron-rhodium alloys, and also of the **cobalt-iron alloys** and of the **nickel-iron alloys.** H. Remy and co-workers found that the **ruthenium-rhodium alloys** are very active catalysts in the reaction between hydrogen and oxygen even though rhodium alone is only slightly active, and ruthenium alone is inactive.

E. Tiede and R. Piwonka studied the **alumina rhodium phosphors.** J. J. Berzelius showed that molten **potassium hydrosulphate** attacks the metal at a dull red-heat, forming a soluble sulphate, and this reaction can be utilized in separating rhodium and iridium. J. J. Berzelius also found that the metal is oxidized when heated to redness with a mixture of **potassium hydroxide and nitrate.** H. Weisz observed that rhodium can serve as nuclei in the solarization of **silver bromide** films. E. Tiede and H. Lüders studied the effect of rhodium on luminescent **alumina.**

Some reactions of analytical interest.—A soln. of sodium chloroperrhodite

with **hydrogen sulphide** in the cold slowly forms a brown precipitate of rhodium sesquisulphide; the precipitation occurs more rapidly with warm soln. The precipitate is insoluble in a soln. of ammonium sulphide, but soluble in boiling nitric acid, in aqua regia, or in bromine water. A dark brown precipitate of alkali rhodium sulphide is produced by **alkali sulphide,** and it is decomposed by water. At first, no precipitate is produced by **potassium or sodium hydroxide,** but on standing some time a yellow precipitate of $Rh(OH)_3.H_2O$ separates out. The precipitate is soluble in an excess of alkali lye, and the soln. deposits dark brown $Rh(OH)_3$ when boiled. A soln. of potassium sulphateperrhodite gives a precipitate immediately on adding potash lye; and a soln. of rhodium trichloride gives at first no precipitate with potash lye, but on adding alcohol, the dark brown hydroxide is precipitated. Aq. **ammonia** produces in conc. soln., after standing some time, a yellow precipitate of the chloropentamminochloride soluble in hydrochloric acid. When **potassium nitrite** is warmed with a soln. of sodium chloroperrhodite a sparingly soluble, orange-yellow potassium hexanitritoperrhodite is precipitated; the precipitate is soluble in hydrochloric acid. When boiled with **stannous chloride,** a brown colloidal soln. is formed which develops a fine crimson—recalling purple of Cassius. W. Singleton recommended the reaction with stannous chloride as a test. Black, metallic rhodium is precipitated by **zinc** in acidic soln. by **formic** acid; and **hydrazine sulphate** or **hydrazine hydrate** in alkaline soln., but not in acidic soln. All solid rhodium compounds are reduced to rhodium when heated in a current of **hydrogen.**

V. N. Ivanoff [2] observed that **thiocyanates** give a black precipitate with rhodium salts. V. G. Chlopin found that **benzidine** gives with salts of tervalent rhodium a rose-yellow precipitate; J. H. Yoe, that a brownish-red precipitate is produced with **ammonium aurintricarboxylate.**

Physiological action of rhodium.—G. C. Gmelin [3] said that the toxic action of rhodium salts comes between those of platinum and palladium.

Some uses of rhodium.—G. K. Burgess and co-workers [4] showed that rhodium stiffens laboratory platinum crucibles, and it tends to reduce the loss by volatilization above 900°, so that best quality platinum crucibles "would be platinum containing 3 to 5 per cent. of rhodium, practically free from iron and iridium, and containing no other detectable impurities." These crucibles should be cheaper and lighter than ordinary platinum crucibles. W. Crookes discussed some advantages of rhodium crucibles. H. le Chatelier, and R. B. Sosman employed the rhodium platinum alloy for thermocouples; I. Westermann, for laboratory resistance furnaces; and G. Trömel and F. Wever, for crucibles for investigating oxides at high temp. Rhodium is also employed as a finish for reflectors, and also for the protection of silverware from tarnish. Rhodanized silver is sold in jewellery stores in the United States. G. F. C. Frick recommended rhodium-black as a black for pottery painting, but no particular use has been made of the suggestion. G. Woker discussed the use as a catalytic agent.

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§ 5. The Atomic Weight and Valency of Rhodium

The equivalent weight of rhodium is about 51·5, making the at. wt. of rhodium about 103, if rhodium is *bivalent* in harmony with the ill-defined monoxide, and with the dichloride. H. Reihlen and W. Hühn[1] discussed bivalent rhodium

sulphites. L. Wöhler and W. Müller reported both these compounds, and also products corresponding with *univalent* rhodium, namely, RhCl, and Rh_2O. Rhodium is *tervalent* in the trifluoride, the trichloride, and in the hemitrioxide. The tervalency is confirmed by the analogy between the isomorphous K_3RhCy_6, and the corresponding compounds of cobalt, iron, and chromium; and between the rhodium and aluminium alums. The element is *quadrivalent* in the dioxide, RhO_2. The subject was discussed by H. Kauffmann, and T. M. Lowry; the relations of the at. wts., by M. Gerber; and the stereochemistry of rhodium salts, by F. G. Mann, A. Werner, E. Leidié, F. M. Jäger, C. E. Wood and S. D. Nicolas, and C. J. Dippell and F. M. Jäger.

The value 103 for the at. wt. of rhodium is in approximate harmony with the sp. ht. rule; with the isomorphous rule for the cobaltic, ferric, and aluminium alums; and with the periodic law in that the properties of rhodium are between those of cobalt and iridium, and between those of ruthenium and palladium. J. J. Berzelius [2] obtained values ranging from 103 to 106 for the at. wt. of impure specimens of rhodium; the results were based on analyses of sodium and potassium chloroperrhodites. T. Thomson also obtained 110·9 from an analysis of the sodium chloroperrhodite. C. Claus adopted 104·4, but methods for purifying the element satisfactorily were then unknown. R. Bunsen, for instance, showed that iridium must have been associated with the early specimens of rhodium.

S. M. Jörgensen reduced rhodium chloropentamminochloride in a steam of hydrogen, and from the ratio $[Rh(NH_3)_5Cl]Cl_2 : Rh$, calculated for the at. wt. 103·06; K. Seubert and K. Kobbé similarly obtained 102·92; A. Hüttlinger, 102·93; and H. Dittmar, 102·91. S. M. Jörgensen determined the ratio $[Rh(NH_3)_5Br]Br_2 : Rh$, and calculated 102·97 for the at. wt.; and C. Renz likewise obtained 102·90. S. M. Jörgensen determined the ratio $[Rh(NH_3)_5Br]Br_2 : 2AgBr$, and calculated 103·14; and K. Seubert and K. Kobbé calculated 103·13 from the ratio $[Rh(NH_3)_5Cl]Cl_2 : AgCl$. The best representative value given by the International Committee on Atomic Weights for 1931 is 102·9.

The **atomic number** of rhodium is 45. A. J. Dempster,[3] F. W. Aston, and F. Allison and E. J. Murphy observed that rhodium has one **isotope**; but F. W. Aston noted that there are probably two isotopes of at. masses 185 and 187, occurring in the percentage abundances 38 and 62, respectively. J. H. Bartlett studied the subject—*see* palladium. The **electronic structure,** according to N. Bohr, and E. C. Stoner, is (2) for the *K*-shell; (2, 2, 4) for the *L*-shell; (2, 2, 4, 4, 6) for the *M*-shell; (2, 2, 4, 4, 3) for the *N*-shell; and (2) for the *O*-shell. The subject was studied by H. Perlitz, P. D. Foote, W. Hulme-Rothery, H. Lersheim and R. Samuel, H. J. Walke, H. Schüler and T. Schmidt, and S. Kato. Neither E. Rutherford and J. Chadwick, nor H. Pettersson and G. Kirsch have observed the **atomic disruption** of rhodium by bombardment with the α-rays.

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§ 6. The Oxides of Rhodium

According to J. J. Berzelius,[1] and T. Wilm, when ruthenium is heated to bright redness in contact with air, there is a rapid increase in weight until **rhodium monoxide,** RhO, is formed. The increase in weight then proceeds more slowly until the product contains Rh_5O_6. According to C. Claus, these products are mixtures of the hemitrioxide and metal, and he obtained an analogous compound by heating the hydrated hemitrioxide to dull redness; and H. St. C. Deville and H. Debray, by cupelling at a white heat an alloy of rhodium and lead. E. Leidié was unable to obtain products of constant composition either by roasting the metal, or by decomposing the hemitrioxide. The grey product obtained at a given temp. gives off oxygen if the temp. is raised, and gains oxygen if the temp. is lowered. Hence, E. Leidié was unable to confirm the existence of rhodium monoxide. A. Gutbier and co-workers observed that the product obtained at temp. between 600° and 1000° is always the hemitrioxide, and that the rate of oxidation increases rapidly with temp. as indicated in connection with the action of oxygen on rhodium—*vide supra*. The so-called monoxide is a mixture of hemitrioxide and metal. This product, said E. Leidié, is insoluble in all the common acids, and in aqua regia. F. M. Jäger discussed the sp. ht. L. Wöhler and W. Müller observed that in the dissociation of rhodium hemitrioxide prepared by heating the trichloride in oxygen at a temp. exceeding 750°, both rhodium monoxide, RhO, and **rhodium hemioxide,** Rh_2O, are formed. The products can be separated by levigation. The vap. press. curves show that at atm. press., in oxygen, the hemitrioxide decomposes at 1113°, the monoxide at 1121°, and the hemioxide at 1127°. F. M. Jäger discussed the sp. ht. L. Wöhler and co-workers found the mol. ht. of Rh_2O to be $C=17{\cdot}355+0{\cdot}00647\theta$, and for RhO, $C=11{\cdot}351+0{\cdot}005530\theta$; and the corresponding heats of formation, 22·70 Cals. and 21·72 Cals. respectively. L. Wöhler and N. Jochum gave for the heat of formation of Rh_2O, 22·7 Cals.; and for RhO, 21·72 Cals.

J. J. Berzelius mentions some other products besides Rh_5O_6 or $3RhO.Rh_2O_3$, namely, Rh_4O_5 or $2RhO.Rh_2O_3$, obtained as a hydrate by the action of boiling potash lye on the 4 : 5 chloride; and Rh_8O_{11} or $2RhO.3R_2O_3$, obtained as a hydrate by the action of an excess of sodium carbonate and potassium chloroperrhodite at a red-heat. There is nothing here to show that these products are chemical individuals. E. Leidié observed that if the hydrated hemitrioxide is heated to redness, there is formed a product corresponding with **rhodium tritatetroxide,** Rh_3O_4—*rhodium perrhodite*, $Rh(RhO_2)_2$. It is insoluble in acids and alkali lye; and is reduced to metal when heated in hydrogen.

C. Claus, and J. J. Berzelius reported **rhodium hemitrioxide,** Rh_2O_3, or **rhodium sesquioxide,** to be formed by the action of heat on the hydrate. The water is retained with great tenacity, and requires an hour's ignition to drive it off; no oxygen is given off during the dehydration. C. Claus prepared this oxide by roasting the nitrate; and E. Frémy, by oxidizing the trichloride in oxygen, or by potassium nitrate or chlorate. L. Wöhler and W. Müller prepared the hemitrioxide by heating rhodium trichloride in oxygen at about 800°. L. Wöhler and N. Jochum gave for the mol. ht. of Rh_2O_3, $C=24{\cdot}504+0{\cdot}013800\theta$, and the heat of

formation, 68·30 Cals. According to A. Gutbier and co-workers, when rhodium is heated in air or oxygen, between 600° and 1000°, rhodium hemitrioxide is formed as a greyish-black powder which, according to W. Zacharisen, G. Lunde, and V. M. Goldschmidt and W. Zacharisen, has a rhombohedral lattice with a=5·47 A., and α=55° 40′, and mol. vol., 52·1. A. Gutbier and co-workers observed that the oxide decomposes into oxygen and rhodium above 1150°. L. Wöhler and W. Müller found the vap. press., p mm., to be :

	772°	920°	1060°	1100°	1112°	1115°
p . .	14	54	406	660	750	760 mm.

F. M. Jäger discussed the sp. ht. G. Kröger studied the thermal dissociation of the oxide. M. le Blanc and H. Sachse found the electrical conductivity of rhodium oxide is small. A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility is independent of temp. S. Pastorello found the hemitrioxide is stable in a current of sulphur dioxide at temp. 450°, but beyond this, the oxide is reduced to metal. He attributed the decreasing catalytic activity of platinum containing rhodium to the formation of a sesquioxide—*vide* iridium dioxide. C. Claus observed that the product is insoluble in acids and in aqua regia, and it is reduced by hydrogen at a dull red-heat, or, if the oxide be in a very fine state of subdivision, at ordinary temp.

According to J. J. Berzelius, when finely-divided rhodium, mixed with potassium hydroxide and nitrate, is heated, it detonates slightly, takes fire, and swells up to a brown mass of potassium perrhodite. Washing with water extracts most of the alkali, and there remains the *monohydrate*, $Rh_2O_3.H_2O$, contaminated with some alkali. The product may be digested with hydrochloric acid, a little chlorine may be evolved owing to the presence of a little alkali nitrate, and washed with water. J. J. Berzelius also obtained this hydrate by evaporating to dryness an aq. soln. of the alkali chloroperrhodite with an excess of alkali carbonate. The clear mixture gradually opacifies and becomes gelatinous. It is then washed with water. C. Claus obtained the *pentahydrate*, $Rh_2O_3.5H_2O$, as a precipitate by adding not too large a proportion of alkali lye to a soln. of a rhodium salt—say the trichloride. When the red liquor is allowed to stand, it deposits a rose-red precipitate consisting of the pentahydrate and some unchanged rhodium salt. The rose-red colour of the precipitate gradually changes to yellow, and it is then well washed. E. Leidié added that the sulphate should not be employed because it forms a basic sulphate and not the hemitrihydrate. C. Claus also described a *trihydrate*, $Rh_2O_3.3H_2O$, or **rhodium trihydroxide,** $Rh(OH)_3$; the nature of these hydrates has not been established.

According to C. Claus, and J. J. Berzelius, hydrated rhodium hemitrioxide is a lemon-yellow powder, which always retains a trace of the alkali employed as precipitant, and a prolonged washing with dil. acid does not remove all the alkali. When the hydrated oxide is heated, it loses water and oxygen, forming a black powder which C. Claus assumed to be the anhydrous hemitrioxide, but E. Leidié's analyses corresponded with Rh_3O_4. Freshly-precipitated hydrate of rhodium hemitrioxide was found by C. Claus to dissolve in conc. potash lye, and to be precipitated again when the soln. is diluted with water ; but if chlorine be passed through the soln. a dark green, oxidized precipitate is formed. The composition of the precipitate is uncertain, and C. Claus found it to be round about Rh_3O_5, or $Rh_2O_3.RhO_2$. The freshly-precipitated hydrate also dissolves readily in the ordinary mineral and organic acids, and less readily in conc. boric, phosphoric, and tartaric acids. F. Bullnheimer said that rhodium is reduced to metal by glycerol. A soln. of the freshly-precipitated hydrate in sulphurous acid furnishes a white, crystalline mass of *rhodium sulphite*, $Rh_2(SO_3)_3.6H_2O$. The ordinary salts of rhodium are derived from this oxide. The soln. of the hydroxide in alkali lye was assumed by J. J. Berzelius, and by H. V. Collet-Descotils to contain *alkali perrhodite.*

S. M. Jörgensen obtained **rhodium hexamminohydroxide,** $[Rh(NH_3)_6](OH)_3$, by adding moist silver oxide to a soln. of the chloride. The liquid is strongly alkaline, and with acids forms salts of the hexammine. S. M. Jörgensen also prepared **rhodium aquopentamminohydroxide,** $[Rh(NH_3)_5(H_2O)](OH)_3$, in soln. by the action of moist silver oxide on the corresponding chloride. The strongly alkaline soln. forms the corresponding salts with acids, and at a higher temp. forms the aquopentammines.

J. J. Berzelius, and C. Claus prepared **rhodium dioxide,** RhO_2, by heating to redness a mixture of finely-divided rhodium and potassium hydroxide and nitrate, washing the product first with water, then with hydrochloric acid, and finally drying it at 100° in an inert atm.—say, of carbon dioxide. J. J. Berzelius said that the colour is greyish-green, but C. Claus showed that traces of iridium must have been present, since, with purified rhodium, the colour is dark brown, and that the analysis agrees with RhO_2. The brown or black oxide is insoluble in acids and in alkali lye. L. Wöhler and K. F. A. Ewald observed that rhodium dioxide cannot be obtained anhydrous; attempts to dehydrate the hydrated dioxide furnish the anhydrous sesquioxide. Rhodium dioxide can be obtained in its hydrated form only by the use of strong oxidizing agents, but quantitatively only by anodic oxidation in conc. alkaline soln. Fusion processes gave only hydrated sesquioxide, whilst chlorine in alkaline soln. gives a hydrated dioxide contaminated with the tervalent oxychloride. S. Pastorello said that the oxide decomposes at 450°.

C. Claus prepared the *dihydrate*, $RhO_2.2H_2O$, or **rhodium tetrahydroxide,** $Rh(OH)_4$, by passing chlorine into a soln. of freshly-precipitated hydrated hemitrioxide in conc. potash lye. The precipitated dihydrate is green, and the supernatant liquor is coloured violet-blue. The production of this blue colour was recommended as a recognition test for rhodium by E. P. Alvarez. C. Claus believed that the green precipitate is a hydrated *rhodium hemipentoxide*, $Rh_2O_5.nH_2O$. E. Demarçay obtained the dihydrated rhodium dioxide by oxidizing sodium chloroperruthenite with hypochlorites, and S. M. Jörgensen similarly, by oxidizing rhodium chloropentamminochloride. A. Joly and E. Leidié obtained a green, anodic deposit of the hydrate by electrolyzing a soln. of an alkali rhodium oxalate or of a double chloride in the presence of an excess of oxalic acid. The hydrated dioxide is insoluble in water; and with hydrochloric acid it passes into soln. with the evolution of chlorine.

According to J. J. Berzelius, when finely-divided rhodium mixed with potassium hydroxide and a little nitrate is ignited, and the cold product washed with cold water, there remains **potassium rhodite,** as a flea-brown powder which gives up its alkali when washed with nitric or sulphuric acid. A. Joly and E. Leidié found that when the alkali nitrites are heated to 360°, the decomposition products are indefinite, but in vacuo, between 440° and 520°, when the evolution of gas has ceased, potassium rhodium nitrite furnishes **potassium hexarhodate,** $K_2O.6RhO_2$; and E. Leidié added that the formation of this salt shows that rhodium dioxide has acidic properties like the corresponding perchromites (or chromites), percobaltites, and permanganites. A. Joly and E. Leidié likewise prepared **sodium octorhodate,** $Na_2O.8RhO_2$; and **barium hexarhodate,** $BaO(6RhO_2)_2$.

C. Claus observed that the violet-blue liquid, formed when chlorine is passed into a soln. of freshly-precipitated, hydrated rhodium hemitrioxide, contains **potassium perrhodite.** When the alkaline soln. is neutralized with nitric acid, there is formed a flocculent, blue precipitate of **rhodium trioxide,** RhO_3. It dissolves in hydrochloric acid with the evolution of chlorine. The blue colour of the soln. of potassium rhodate was found by E. P. Alvarez to be destroyed by sodium dioxide, potassium persulphate, and sulphurous acid. If the gases evolved by heating a mixture of hydrochloric acid and potassium chlorate are passed into a soln. of a rhodium salt in sodium hydroxide, the liquid becomes yellowish-red, then red, and finally, a green precipitate forms. The precipitate dissolves, forming a blue soln.—*Claus' blue solution*—which contains **sodium perrhodate.**

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§ 7. The Rhodium Halides

O. Ruff [1] observed that rhodium is scarcely attacked by fluorine at a red-heat and was unable to prepare a fluoride of rhodium directly; but by the action of dry fluorine on dry rhodium chloride, E. Ascher, and O. Ruff and E. Ascher were able to prepare **rhodium trifluoride,** RhF_3. The reaction begins between 400° and 500°, and to obtain a complete transformation, the temp. is raised to 500° or 600°. The fluorine is then displaced by dry nitrogen. The trifluoride is a red, crystalline powder which is not hygroscopic, and which is stable. The **crystals** belong to the rhombic system having the axial ratios $a:b:c=1{\cdot}355:1:0{\cdot}916$, and the X-radiograms indicate that there are 4 mols. per unit cell. J. A. A. Ketelaar, on the other hand, said that the salt is hexagonal and isomorphous with the corresponding fluorides of aluminium, iron, cobalt, and palladium. There are 3 mols. in unit cell, and the cell constants are $a=4{\cdot}88$ A., and $c=6{\cdot}81$ A. The distance between two fluorine atoms is 2·44 A. L. Pauling, F. Ebert, and W. Nowacki discussed the subject. E. Ascher, and O. Ruff and E. Ascher found that the calc. **specific gravity** is 5·67, and the observed sp. gr. is 5·38. The trifluoride volatilizes above 600°. The salt is reduced in **hydrogen** at about 70°; and when heated in air it darkens and forms an oxide; it is very stable towards **water,** and it is almost insoluble even in boiling water; in steam, at 250°, the salt is hydrolyzed to black rhodium trihydroxide, which is soluble in hydrochloric acid. The trifluoride above 600° is converted by **fluorine** into a sublimate of higher fluoride, but the yield is so small, and so impure, that it was not possible to decide whether the product is **rhodium tetrafluoride,** RhF_4, or **rhodium pentafluoride,** RhF_5. The trifluoride is scarcely affected by **iodine;** boiling conc. **hydrochloric acid** scarcely attacks the trifluoride; at 100°, 40 per cent. **hydrofluoric acid** dissolves it sparingly with slow hydrolysis; **sulphur** has no perceptible action; **hydrogen sulphide** at a dull red-heat forms probably the monosulphide, insoluble in acids; when heated with **sulphur dioxide,** the salt is slowly blackened and reduced to rhodium; hot conc. **sulphuric acid** slowly decomposes the salt with the evolution of hydrogen fluoride; and when strongly heated with **ammonia,** it forms ammonium fluoride and rhodium; there is scarcely any attack by boiling, conc. **nitric acid;** there is a detonation when the salt is heated with red **phosphorus;** **carbon** has scarcely any action; at a red-heat, crystalline **silicon** reacts with the salt; **sodium** burns when heated with the salt; **magnesium** reacts explosively; **aluminium** burns with a white flame; **iron** reacts at a red-heat; **rhodium** has no perceptible action; a boiling

33 per cent. soln. of **sodium hydroxide** has scarcely any action, and in the presence of reducing agents, finely-divided rhodium, soluble in aqua regia, is formed; molten **sodium carbonate** forms sodium fluoride and rhodium hemitrioxide, which is insoluble in acids and in aqua regia.

J. J. Berzelius reported that **rhodium dichloride,** $RhCl_2$, is formed on passing chlorine over heated rhodium, or, according to L. R. von Fellenberg, over heated rhodium monosulphide. C. Claus, and E. Leidié questioned the chemical individuality of these products. A. Gutbier and A. Hüttlinger observed that chlorine begins to act on rhodium at 250°, forming the trichloride; E. Leidié said that the attack is very slow at 350° to 440°. L. Wöhler and W. Müller added that the reaction occurs between 300° and 968°, and that below 948°, the trichloride is formed, but between 965° and 970°, reddish-brown rhodium dichloride, as well as **rhodium monochloride,** RhCl, are formed. They can be separated by levigation in carbon tetrachloride, the dichloride is the lighter, and the monochloride is the heavier. If the chlorination occurs at 950° to 955°, the lightest fraction is the dichloride, and the heaviest, the trichloride. In chlorine at atm. press., the vap. press. curves show that the trichloride decomposes at 948°, the dichloride at 958°, and the monochloride at 964°. J. J. Berzelius, and L. R. von Fellenberg said that the dichloride is a greyish-red, dingy violet, or rose-red powder. V. M. Goldschmidt, and G. Bruni and A. Ferrari discussed the possible structure of the space lattice of the dichloride. J. J. Berzelius, and L. R. von Fellenberg found that what they considered to be the dichloride may be gently heated without decomposition, but in hydrogen it forms hydrogen chloride and rhodium; it is not altered when heated in chlorine; it is not affected by boiling soln. of potassium hydroxide or carbonate; and it is insoluble in water, hydrochloric acid, and nitric acid.

J. J. Berzelius thought that he had formed a complex chloride, $RhCl_2.RhCl_3$; by reducing alkali chloroperrhodite in hydrogen, and passing chlorine over the product until its weight is constant. There is nothing here to show that the product is partially-chlorinated rhodium. C. Claus showed that neither the dichloride nor J. J. Berzelius' Ru_2Cl_5 can be obtained as chemical individuals by this process, and that the products are mixtures of rhodium and its trichloride. C. Claus was also unable to chlorinate rhodium completely to **rhodium trichloride,** $RhCl_3$, and E. Leidié obtained the best results with finely-divided rhodium, and rhodium black; the latter gave the better results at a red-heat. The products were about 2 per cent. short of chlorine for the trichloride. The proportion is less the higher is the temp. The inference is that the trichloride partially dissociates at a red-heat: $2RhCl_3 \rightleftharpoons 2Rh+3Cl_2$. A. Gutbier and A. Hüttlinger observed that the reaction with chlorine begins at about 250°. L. Wöhler and W. Müller found the vap. press., p mm., of the trichloride to be

	765°	825°	902°	915°	942°	945°	947°	948°
p .	66	134	390	459	674·5	706	736	760 mm.

The anhydrous salt and the tritadihydrate were prepared by M. Delépine. E. Leidié observed that L. R. von Fellenberg's method of preparing the chloride, by heating rhodium sulphide in chlorine was unsatisfactory because when the temp. is high enough to eliminate the sulphur, the chloride is partly decomposed. A sample of sulphide after being heated to dull redness in chlorine for 8 hrs. still retained 0·81 per cent. of sulphur. If hydrated rhodium trichloride is heated in dry nitrogen at 440°, the hemitrioxide, and hydrogen chloride are formed, but if the hydrate be heated to 440° in chlorine, it furnishes the anhydrous trichloride. If hydrated ammonium chloroperrhodite is heated to 440° in dry nitrogen, the products are the hemitrioxide, and hydrogen and ammonium chlorides. E. Leidié obtained the anhydrous trichloride by heating the $RhSn_3$-alloy between 360° and 440° in a current of chlorine. Stannous chloride volatilizes. The product is allowed to cool completely in a current of chlorine, and this gas is then displaced

by carbon dioxide. S. M. Jörgensen obtained the anhydrous trichloride by heating rhodium chloropentamminochloride in chlorine.

Anhydrous rhodium trichloride is a brick-red, or brownish-red powder. F. Ebert found the crystals have trigonal rhombohedral symmetry, there is 1 mol. in unit cell, and $a=4{\cdot}898$ A., and $c=6{\cdot}81$ A., for trigonal symmetry, and for rhombohedral symmetry, $a=3{\cdot}617$ A., and $\alpha=84°\ 48'$, the distance between the Rh- and F-atoms is 1·98 A., and the calculated sp. gr. is 5·64, when the observed value is 5·38. S. M. Karim and R. Samuel studied the absorption spectrum; and B. Cabrera and H. Fahlenbrach, the paramagnetism. W. Hampe found that the chloride fused at a dull red-heat is a good conductor of electricity and decomposes with such vigour as to take fire; chlorine is evolved from the carbon anode, and rhodium separates at the platinum wire cathode. F. C. Phillips observed that **hydrogen** reduces the trichloride at a dull red-heat, forming the metal, the reducing action takes place as low as 190°. E. Leidié found that the anhydrous trichloride is insoluble in **water**; and that when heated in a rapid current of **chlorine** at a bright red-heat, a deposit the colour of peach-blossom forms on the cold part of the tube—it is a product of the dissociation of the chloride, and its composition is variable, but it approximates $RhCl_3$. C. Claus found that at a bright red-heat the trichloride is gradually reduced to metal, which, according to H. Debray, is nearly free from chlorine. L. A. Welo and K. Baudisch studied the magnetic properties. For the dissociation press. of the trichloride, *vide supra*. When heated in chlorine with an alkali chloride, a complex salt is formed. The anhydrous trichloride is insoluble in **acids.** It dissolves in, and is decomposed by, soln. of **alkali hydroxides,** and the liquid behaves like a soln. of rhodium hemitrioxide in alkali lye. W. Manchot and G. Lehmann observed that carbon monoxide lowers the temp. at which halogen is evolved, but no carbonyl chloride is formed; but, as indicated below, $RhCl_2.RhO.(CO)_3$ can be prepared. Here, the nitrosyl and carbonyl radicles are interchangeable, forming, according to W. Manchot and W. Pflaum, **rhodium trinitrosyloxydichloride,** $RhCl_2.RhO.(NO)_3$. According to C. Claus, the anhydrous trichloride dissolves in conc. soln. of **potassium cyanide, alkali tartrates,** and **alkali oxalates,** forming in each case a complex salt. F. C. Phillips studied the action of the trichloride on **hydrocarbons.**

J. J. Berzelius prepared a soluble hydrate, probably the *tetrahydrate*, $RhCl_3.4H_2O$, by adding hydrofluosilicic acid, not in excess, to a soln. of potassium chloroperruthenite, evaporating the filtered soln. to dryness, extracting the mass with water, and again evaporating the hydrochloric acid soln. to dryness to drive off the silicon fluoride. C. Claus prepared it by evaporating a soln. of the hydrated hemitrioxide in hydrochloric acid, but, as noted by J. J. Berzelius, and W. H. Wollaston, the soln. does not furnish crystals of the salt. The product, also, is contaminated with alkali originally employed to precipitate the hydrated hemitrioxide. H. Debray recommended extracting the mass with alcohol which dissolves the trichloride, evaporating the extract to drive off the alcohol, dissolving the residue in water, and evaporating as before. E. Leidié added that the alcohol employed should be free from reducing agents. G. Goloubkine found that hydrochloric acid saturated with chlorine readily dissolves spongy rhodium forming the trichloride. E. Leidié recommended preparing the hydrated trichloride as follows:

A current of chlorine is passed over a fused mixture of finely-divided rhodium and an excess of sodium chloride, and the product dissolved in twice its weight of water. Conc. hydrochloric acid is added, and the liquid is allowed to stand for 24 hrs. to allow the sodium chloride to crystallize out. The clear liquid, at 0°, is saturated with hydrogen chloride, and the product allowed to stand several days at 0° to remove the remaining sodium chloride. The decanted liquid is gently evaporated to a syrup, and allowed to stand in a desiccator over potassium hydroxide to remove the uncombined water.

C. Claus said that the hydrated trichloride is tetrahydrated, but E. Leidié added that the brick-red, deliquescent hydrate is amorphous and does not correspond with any definite hydrate. When heated it breaks down into hydrogen

chloride and rhodium hemitrioxide—at 90° to 95°, it retains 4 mols. of water, and 2 mols. of HCl; at 100°, it loses both water and hydrogen chloride; and at 175°, it is completely dehydrated. When heated in a current of hydrogen chloride at 180°, the trichloride is dehydrated, and it can take up water again, but at above that temp., say at 360°, the trichloride becomes insoluble in water, and at 440°, the transformation, in a current of chlorine, is complete. The hydrated trichloride is freely soluble in **water.** According to J. J. Berzelius, the soln. in water is rose-red, and in **hydrochloric** acid the soln. is yellow and does not recover its red colour until the acid has been expelled by evaporation. H. Rose noted that **potassium iodide** darkens a soln. of the trichloride, and after a time gives a slight precipitate. According to N. W. Fischer, **hydrogen sulphide** gives a brown precipitate—soluble in hydrochloric acid—with soln. containing at least 1 part of rhodium in 2000 parts of liquid; J. J. Berzelius added that the precipitate forms readily in warm soln., and H. Rose, that the precipitate forms after the mixture has stood some time. H. V. Collet-Descotils observed that **ammonium sulphide** very slowly forms a brown precipitate of sulphide, more rapidly if the soln. is heated, and J. J. Berzelius added that the precipitate is soluble in excess. The hydrated trichloride is transformed by **sulphuric acid** into sulphate. G. Sailer found that **sodium hyposulphite** forms a sulphite, $Na_6[Rh_4(SO_3)_7].12H_2$. J. J. Berzelius found that aq. **ammonia,** or **ammonium carbonate,** produces a lemon-yellow precipitate of the ammonium chloroperrhodite which forms a yellow soln. with hydrochloric acid. S. M. Jörgensen noted that rhodium chloropentamminochloride is formed in ammoniacal soln. W. Manchot said that when heated in carbon monoxide, a sublimate of a carbonyl is formed, and W. Manchot and J. König found that the anhydrous chloride does not react with dry carbon monoxide, but the hydrated chloride, preferably at 150°, forms **rhodium tricarbonyloxydichloride,** $Rh_2OCl_2(CO)_3$, which melts at 125·5°, and decomposes at 300°. W. H. Wollaston also observed that the hydrated trichloride is freely soluble in alcohol, and that the soln. is rose-red. The salt is insoluble in ether. P. Claesson observed that alcoholic soln. of the trichloride give a yellow, amorphous precipitate with mercaptan. H. Rose observed that no precipitates were produced in aq. soln. of the trichloride by **mercuric cyanide, potassium cyanide, ferrocyanide,** or **ferricyanide, oxalic acid,** or **gallic acid.** W. H. Wollaston noted that some **metals**—copper, zinc, mercury, and iron—precipitate rhodium as a black powder from the aq. soln., but not so with silver. N. W. Fischer observed that tin gives a brown precipitate. J. J. Berzelius stated that a soln. of **potassium hydroxide,** or **carbonate,** on evaporation, precipitates yellowish-brown, gelatinous, hydrated hemitrioxide; and H. V. Collet-Descotils, that **lime-water** also yields a similar precipitate, even in the dark. H. Rose observed that the precipitates were observed with **sodium phosphate, ammonium** or **sodium chlorides,** or with **potassium chromate.** J. J. Berzelius noted that **stannous chloride** gives a precipitate of the hydrated oxide, soluble in acids; and N. W. Fischer, that soln. of stannous chloride give with conc. soln. of rhodium trichloride a brownish-yellow precipitate or a brown soln., with more dil. soln., a yellow precipitate, and with soln. having 1 part of rhodium in 1500 parts of liquid, a yellow coloration. A soln. of **ferrous sulphate** precipitates a yellow powder from soln. of rhodium trichloride and ammonia; the powder is soluble in hydrochloric acid.

L. N. Vauquelin, and J. J. Berzelius studied the action of ammonia on soln. of ammonium trichloroperrhodite, and obtained an ammine. S. M. Jörgensen prepared **rhodium hexamminochloride,** $[Rh(NH_3)_6]Cl_3$, by heating at 100° rhodium chloropentamminochloride for a long time in a closed vessel, and adding hydrochloric acid. The precipitate is anhydrous, but if obtained by gentle evaporation, the *dihydrate* is formed. G. Beck studied the ionization of the salt. According to S. M. Jörgensen, the anhydrous salt furnishes lustrous, rhombic prisms; the prismatic crystals of the dihydrate are efflorescent. According to C. D. West, the crystals are cubic. S. M. Jörgensen observed that both salts are soluble in

water, and insoluble in hydrochloric acid, but if heated with conc. hydrochloric acid, the chloropentamminochloride is formed. The aq. soln. gives characteristic precipitates with gold chloride, mercuric chloride, potassium dichromate, etc.; and if treated with platinic chloride there are formed two **rhodium hexammino-chloroplatinates,** $[Rh(NH_3)_6]Cl_3.PtCl_4.\frac{1}{2}H_2O$, and $2[Rh(NH_3)_6]Cl_3.3PtCl_4.6H_2O$. J. A. Christiansen and R. W. Asmussen studied the magnetic properties of the complex rhodium compounds. For the action of various reagents, *vide infra,* the hexamminonitrate. A. Werner prepared **rhodium trisethylenediaminochloride,** $[Rh\,en_3]Cl_3.2\frac{1}{2}H_2O$, by the interaction of 45 grms. of ethylenediammine monohydrate with 100 grms. of sodium chloroperrhodite. The salt cannot be separated from sodium chloride by recrystallization, and it is therefore converted into iodide by treatment with sodium iodide. The iodide is purified by crystallization, and a soln. is shaken with freshly-precipitated silver chloride, and filtered. The soln. furnishes cubic crystals which lose their water of crystallization at 120°. F. M. Jäger said that the crystals of the racemic compound are *trihydrated,* and that the crystals are strongly refracting, ditetragonal prisms with the axial ratio $a:c=1:0{\cdot}6730$, and are isomorphous with those of the corresponding cobaltic salt. E. Rosenbohm studied the magnetic susceptibility. A. Werner prepared **rhodium** ***d*****-trisethylenediaminochloride,** with $[\alpha]_D=78°$, and **rhodium** ***l*****-trisethylene-diaminochloride,** with $[\alpha]_D=-80°$. F. M. Jäger also prepared these salts and examined the crystals. J. Lifschitz and E. Rosenbohm studied the optical properties. M. Delépine prepared **rhodium-dichloroquaterpyridine,** $[Rhpy_4Cl_2]$, represented by a complex with $[Rhpy_2Cl_4]$; **rhodium dichloroaquotrispyridine,** $[Rhpy_3(H_2O)Cl_2]$, represented by a complex with $[Rhpy_2Cl_4]$; **rhodium trichloro-trispyridine,** $[Rhpy_3Cl_3]$; **rhodium trichloraquobispyridine,** $[Rhpy_2(H_2O)Cl_3]$; **rhodium tetrachlorobispyridines,** $[Rhpy_2Cl_4]$, in its cis- and trans-forms, represented by potassium, ammonium, silver, and pyridinium salts as well as complexes with $[Rhpy_3(H_2O)Cl_2]$, and with $[Rhpy_4Cl_2]$; and **rhodium nitratotrichloro-pyridines,** $[Rhpy_2(NO_3)Cl_3]$—*vide infra.* M. Delépine and R. Charonnat prepared dextro- and lævo-forms of **cobaltic rhodium trisethylenediaminochloride,** $[Co_{0{\cdot}5}Rh_{0{\cdot}5}\,en_3]Cl_3$, may be in solid soln. C. J. Dippel and F. M. Jäger prepared the dextro- and lævo-forms of $\alpha\beta\delta$- and $\beta\beta\delta$-ammopentane, **rhodium trisamino-pentanochloride,** $[Rhptn_3]Cl_3.2H_2O$. F. M. Jäger and H. B. Blumendal prepared **rhodium trisdiaminocyclopentanochloride,** $[Rh(C_5H_{12}N_2)_3]Cl_3.2H_2O$. S. M. Jörgensen obtained **rhodium aquopentamminochloride,** $[Rh(NH_3)_5(H_2O)]Cl_3$, by heating the chloropentamminochloride for a long time with a large excess of aq. ammonia, and crystallizing the soln. in an atm. of ammonia, otherwise some of the aquo-salt will revert to the chloro-salt. It is also produced by saturating the hydroxide with hydrochloric acid. The yellowish-white crystals are soluble in water, and the salt has a tendency to form the chloropentammino-salt. This transformation occurs at 100°, or in the cold in the presence of hydrochloric acid. J. N. Brönsted and K. Volqvartz studied the acidic dissociation of this salt. V. V. Lebedinsky and co-workers prepared **rhodium triamminotrichloride,** $Rh(NH_3)_3Cl_3$, complexes with **thiocarbamide**—*e.g.* $[RhR_3Cl_3]$, and $[RhR_5Cl]Cl_2$, where R denotes $CS(NH_2)_2$; and with **methyl cyanide,** $M_2[Rh(CH_3Cy)Cl_5].H_2O$, where M denotes NH_4, Rb, Cs, and Ag; and F. M. Jäger and J. A. van Dijk, complexes with **2,2′-bipyridyl.**

C. Claus prepared **rhodium chloropentamminochloride,** $[Rh(NH_3)_5Cl]Cl_2$, by boiling with an excess of ammonia a soln. of rhodium trichloride, and ammonium chloroperrhodite, filtering the hot soln., evaporating to dryness, extracting the product with boiling water, and allowing the hot liquid to cool when it deposits the salt in crystals which are to be washed with dil. acid, and dried at 100°. To avoid the formation of the aquopentammine, it is advisable to precipitate the salt from a soln. acidified with hydrochloric acid which dissolves the aquo-salt. C. Claus, and S. M. Jörgensen observed that instead of using the trichloride, the hydrochloric acid soln. of the rhodium-zinc alloy can be employed. According to

H. Töpsöe, the pale yellow, crystalline powder consists of rhombic prisms isomorphous with the corresponding ammines of cobalt and chromium. C. D. West found that the crystal structure is rhombic with a=13·32 A., b=6·71 A., and c=10·42 A. The salt is stable at ordinary temp., but decomposes at about 200°. Heated in hydrogen, it forms rhodium. The salt is sparingly soluble in cold water, but freely soluble in boiling water. J. N. Brönsted and A. Petersen studied the solubility of the salt in various aq. soln. of different salts. S. F. Schemtschuschny found that, at 25°, a sat. aq. soln. contains 0·828 per cent. of the salt; and when the solvent is 2·61, 4·51, and 10·56 per cent. hydrochloric acid, the values are, respectively, 0·086, 0·021, and 0·007 per cent. Dry chlorine at a red-heat forms anhydrous rhodium trichloride. This salt is a convenient source of the other chloropentammines, since hydrobromic and hydriodic acids form the corresponding halides; silver nitrate removes only two-thirds of the chlorine from cold soln., but all the contained chlorine is completely precipitated from hot soln. Oxidizing agents act on the aq. soln. forming rhodium dioxide; zinc decomposes the acidic or alkaline soln. to form rhodium; soda lye at 100° forms aquopentammines without liberating ammonia; aq. ammonia acts similarly and platinic chloride furnishes yellowish-brown crystals of **rhodium chloropentamminochloroplatinate,** $[Rh(NH_3)_5Cl]PtCl_6$. If the chloropentamminochloride be treated with silver oxide, a soln. of **rhodium chloropentamminohydroxide,** $[Rh(NH_3)_5Cl](OH)_2$, and a precipitate of silver chloride are formed. The strongly alkaline soln. absorbs carbon dioxide from the atmosphere, and it displaces ammonia from the ammonium salts; it dissolves alumina, but not the oxides of copper or silica, but behaves towards them like alkali lye; and it unites with acids to form the corresponding salts. The hydroxide is known only in soln., because it is transformed into the aquopentammine—slowly in the cold, rapidly at 100°, so that the soln. then gives a precipitate with silver nitrate. S. M. Jörgensen obtained **rhodium dichloroquaterpyridinechloride,** $[Rhpy_4Cl_2]Cl$, by the action of pyridine on a hot soln. of rhodium trichloride. Yellow prisms are deposited when the liquid cools. J. A. Christiansen and R. W. Asmusun examined the magnetic properties of the salt. S. M. Jörgensen observed that platinic chloride forms **rhodium dichloroquaterpyridinechloroplatinate,** $[Rhpy_4Cl_2]_2PtCl_6$. If the chloride be triturated with freshly-precipitated silver oxide, there is formed **rhodium dichloroquaterpyridinehydroxide,** $[Rhpy_4Cl_2](OH)$. P. Poulenc studied the chloropyridines. F. G. Mann and W. J. Pope prepared **rhodium chloro-$\beta\beta'\beta''$-triaminotriethylamine,** $3RhCl_2.2N(C_2H_4.NH_2)_3.6HCl.6H_2O$, and $2RhCl_2.N(C_2H_4.NH_2)_3.4HCl$. F. G. Mann prepared **rhodium dichlorobisdiaminodiethylaminohydrochloride rhodiochloride,** $[Cl_2Rh\{CH_2N.C_2H_4)_2NH.HCl\}_2Cl.RhCl_3$. L. A. Tschugaeff and W. Lebedinsky prepared **rhodium bisdimethylglyoximodiamminochlorides,** $[Rh(NH_3)_2D_2H_2]Cl.5H_2O$; **rhodium bisdimethylglyoximodiamminochloroplatinate**; and **dichlorobisdimethylglyoximorhodous acid,** $H[RhD_2H_2Cl_2]$; **ammonium dichlorobisdimethylglyoximorhodite,** $(NH_4)[RhD_2H_2Cl_2].H_2O$; and **guanidinium dichlorobisdimethylglyoximorhodite.** F. M. Jäger studied the **rhodium 2 : 2'- dipyridylchlorides.**

Rhodium trichloride forms two classes of salts with the alkali and ammonium chlorides, namely, alkali **hexachloroperrhodites,** which, according to A. Duffour, are isomorphous with the corresponding salts of iridium, and alkali **pentachloroperrhodites,** which resemble the corresponding salts of iridium and ruthenium. M. Delépine and P. Boussi studied the dehydration of the chloroperrhodites, but obtained no evidence of the presence of polymerized water molecules.

C. Claus, T. Wilm, and W. Keferstein observed that **ammonium hexachloroperrhodite,** $(NH_4)_3RhCl_6.1\frac{1}{2}H_2O$, is formed by slowly evaporating in the cold a soln. of rhodium trichloride and an excess of ammonium chloride. The same salt was prepared by E. Leidié, and T. Wilm, by allowing ammonium chloronitratoperrhodite to stand in contact with water; E. Leidié, by warming ammonium nitritoperrhodite with conc. hydrochloric acid; and A. Gutbier and A. Hüttlinger,

by saturating an aq. soln. of potassium pentachloroperrhodite with hydrogen chloride to precipitate most of the potassium chloride, and then adding ammonium chloride. The red crystals are freely soluble in water, but not in alcohol; they do not effloresce in air; and when heated to redness, rhodium remains. A. Duffour said that this salt is isomorphous with the potassium salt, and with the corresponding salts of iridium. O. E. Zvyagintzeff obtained addition products—*e.g.*, $RhCl_6(NH_3)_4.NH_4NO_3$.

J. J. Berzelius, L. N. Vauquelin, T. Wilm, and C. Claus obtained **ammonium pentachloroperrhodite,** $(NH_4)_2RhCl_5.2H_2O$, from a soln. of the component salts, and A. Gutbier and A. Hüttlinger observed that the *monohydrate* is formed, in red crystals, if theoretical proportions of the component salts are employed. M. Delépine also prepared the monohydrate. C. Claus reported that the *dihydrate* is formed by boiling soln. of the hexachloro-salt. V. V. Lebedinsky prepared $(NH_4)_2.[Rh(NH_3)Cl_5]$, which on hydrolysis forms $(NH_4)_2[Rh(NH_3)Cl(OH)_4]$; also M. Delépine prepared **potassium pentachloroaquoperrhodite,** $(NH_4)_3Rh(H_2O)Cl_5$; **rubidium pentachloroaquoperrhodite,** $Rb_3Rh(H_2O)Cl_5$; **cæsium pentachloroaquoperrhodite,** $Cs_3[Rh(H_2O)Cl_5]$; **ammonium pentachloroaquoperrhodite,** $(NH_4)_3[Rh(H_2O)Cl_5]$; and **silver pentachlorohydroxyperrhodite,** $Ag_3Rh(OH)Cl_5$. F. M. Jäger said that the reddish-black, octahedral crystals of the sodium salt are monoclinic with the axial ratios $a:b:c=1{\cdot}2034:1:1{\cdot}4576$, and $\beta=57°\ 9\frac{1}{2}'$.

A. Gutbier prepared **methylammonium heptachloroperrhodite,** $(CH_3NH_3)_4RhCl_7$; and **ethylenediammonium heptachloroperrhodite,** $(C_2H_6.N_2H_6)_2RhCl_7$.

According to C. Claus, **potassium hexachloroperrhodite,** $K_3RhCl_6.nH_2O$, is obtained from a soln. of potassium chloride and rhodium trichloride, the yellow soln. gradually becomes red, and in a few weeks deposits red crystals of the *hexahydrate* which, on exposure to air, forms the *trihydrate*. The monohydrate was prepared by M. Delépine. E. Leidié did not succeed in preparing C. Claus' salt, but he reported the trihydrate to be formed when potassium rhodium nitrite is treated with warm hydrochloric acid. A. Duffour, however, said that E. Leidié's salt is the monohydrate isomorphous with the corresponding iridium salt. Water decomposes the hexachloro-salt into the anhydrous pentachloro-salt, and for this reason, it is thought that C. Claus' salt was really the pentachloroperrhodite. When the salt is heated in dry hydrogen chloride, the water of crystallization is driven off, and slowly at 360°, rapidly at 440°, a mixture of insoluble, anhydrous rhodium trichloride and of potassium chloride is formed. J. J. Berzelius reported anhydrous **potassium pentachloroperrhodite,** K_2RhCl_5, to be formed when finely-divided rhodium mixed with potassium chloride is heated in a current of chlorine. The mass is extracted with water and crystallized. J. J. Berzelius represented the salt as a hydrate, but E. Leidié could not confirm the presence of water. E. Leidié also prepared this salt by allowing a mixed soln. of rhodium trichloride with an excess of potassium chloride to crystallize. According to H. Dufet, the red crystals are rhombic. E. Leidié found that they are slightly soluble in water, and insoluble in alcohol. M. Delépine and P. Boussi studied the hydrates. C. Claus reported the *dihydrate* to be formed when potassium chloride is added to a soln. of sodium chloroperrhodite. It forms non-efflorescent, brown prisms which are sparingly soluble in water. A. Gutbier and A. Hüttlinger, and K. Seubert and K. Kobbé obtained the *monohydrate* by fusing spongy rhodium with twice its weight of potassium chloride in a stream of chlorine. The aq. extract of the cold mass, on evaporation, furnishes red crystals of the monohydrate; and the mother-liquor, when saturated with hydrogen chloride, deposits crystals of the hexachloro-salt. M. Delépine studied the action of oxalic acid.

A. Gutbier and A. Hüttlinger obtained a red precipitate of **rubidium pentachloroperrhodite,** $Rb_2RhCl_5.H_2O$, by concentrating mixed soln. of rubidium chloride and the potassium pentachloro-salt; and also by concentrating a mixed soln. of the component chlorides in theoretical proportions. A rose-coloured precipitate of **cæsium pentachloroperrhodite,** $Cs_2RhCl_5.H_2O$, was obtained in a similar

manner. M. Delépine prepared **rubidium chloroperrhodite,** $Rb_3RhCl_6.H_2O$; **sodium chloroperrhodite,** $Na_3RhCl_6.12H_2O$; **lithium chloroperrhodite,** $Li_3RhCl_6.12H_2O$, a mixed **sodium lithium chloroperrhodite,** $Li_{1\frac{1}{2}}Na_{1\frac{1}{2}}RhCl_4.12H_2O$; and **ammonium chloroperrhodite,** $(NH_4)_3RhCl_6$. C. Vincent, and C. Friedel discussed **methylammonium hexachloroperrhodite,** $(CH_3.NH_3)_4RhCl_7$; **dimethylammonium hexachloroperrhodite,** $\{(CH_3)_2NH_2\}_3RhCl_6.1\frac{1}{2}H_2O$; and **trimethylammonium hexachloroperrhodite,** $\{(CH_3)_3NH\}_3RhCl_6.4\frac{1}{2}H_2O$.

J. J. Berzelius, W. H. Wollaston, and H. V. Collet-Descotils prepared **sodium hexachlororhodate,** $Na_3RhCl_6.18H_2O$, by heating a mixture of finely-divided rhodium and sodium chloride to redness in a current of chlorine. C. Claus added that there is less risk of particles of rhodium escaping attack if it be first heated in chlorine, the product mixed with the sodium chloride, and again exposed to the chlorine. On extracting the cold mass with water, and evaporating, the *octodecahydrate* crystallizes out. The salt was prepared by V. V. Lebedinsky and I. A. Fedoroff. C. Claus, T. Thomson, and E. Biewend said that the salt contains $24H_2O$; F. M. Jäger, and A. Gutbier and A. Hüttlinger, $12H_2O$; and J. J. Berzelius, and E. Leidié, $18H_2O$. E. Leidié recommended preparing the salt by warming sodium rhodium nitrite with conc. hydrochloric acid. Garnet-red octahedra of the octodecahydrate are formed which effloresce on exposure to air. The crystals are soluble in water, but not in alcohol. F. M. Jäger said that the crystals of the dodecahydrate are octahedral, and belong to the monoclinic system having the axial ratios $a:b:c=1\cdot2034:1:1\cdot4576$, and $\beta=57°\ 9\frac{1}{2}'$. R. Samuel and A. R. Despande studied the absorption spectrum. G. Foussereau found that the electrical conductivity of a soln. of sodium chlororhodate (1 : 100) changes very slowly at ordinary temp. G. Gire observed that the salt begins to dissociate below 600°, and that the m.p. is 904°, the heat of the reaction below 904° is 35·3 Cals., and above that temp., 46·0 Cals. The vap. press., p, in mm. of mercury, is:

	609°	663°	712°	751°	800°	825°
p . .	14·0	30·9	73·3	120	274	460

V. Ipatéeff and V. G. Troneff studied the displacement of rhodium from aq. soln. of the salt by hydrogen under press.; and R. Samuel and M. Uddin, the absorption spectrum of Na_2RhCl_6. G. Sailer observed that sodium hyposulphite furnishes a sodium sulphitorhodate. G. Gire and F. Puche found the dissociation press. of barium hexachlororhodate, $Ba_3(RhCl_6)_2$, to be less than those of rhodium monochloride. The heat of dissociation are 32·9 cals.

W. H. Wollaston, and H. Debray added silver chloride to a soln. of rhodium trichloride, and obtained a precipitate thought to be, not a **silver rhodium chloride,** but a lake of silver chloride coloured by the rhodium salt; the precipitate with mercurous nitrate had the composition **mercurous rhodium chloride,** $RhCl_3.3HgCl$, but it too is considered to be a kind of lake of mercurous chloride coloured by the rhodium salt. The rose-coloured precipitate with a lead salt, observed by C. Claus, is not, as indicated by the analysis, **lead rhodium chloride,** $2RhCl_3.3PbCl_2$, but is a lake of lead chloride tinted by the rhodium salt. O. W. Gibbs obtained a complex salt, **cobaltic hexamminochloroperrhodate,** $[Co(NH_3)_6]RhCl_6$, as an insoluble, pale yellow precipitate which can be utilized in the separation of the platinum metals.

A. Gutbier prepared **dimethylammonium chlororhodate,** $\{(CH_3)_2NH_2\}_3RhCl_6$; **trimethylammonium chlororhodate,** $\{(CH_3)_3NH\}_3RhCl_6$; **ethylammonium chlororhodate,** $(C_2H_5NH_3)_3RhCl_6$; **diethylammonium chlororhodate,** $\{(C_2H_5)_2NH_2\}_3RhCl_6$; **triethylammonium chlororhodate,** $\{(C_2H_5)_3NH\}_3RhCl_6$; ***n*-propylammonium chlororhodate,** $(C_3H_7NH_3)_3RhCl_6$; **iso-propylammonium chlororhodate,** $(C_3H_7NH_3)_3RhCl_6$; **dipropylammonium chlororhodate,** $\{(C_3H_7)_2NH_2\}_3RhCl_6$; **tripropylammonium chlororhodate,** $\{(C_3H_7)_3NH\}_3RhCl_6$; ***n*-butylammonium chlororhodate,** $(C_4H_9NH_3)_3RhCl_6$; **iso-butylammonium chlororhodate,** $(C_4H_9NH_3)_3RhCl_6$; **di-iso-butylammonium chlororhodate,** $\{(C_4H_9)_2NH_2\}_3RhCl_6$;

guanidinium chlororhodate, $(C.NH.NH_2.NH_3)_3RhCl_6$; **propylenediammonium chlororhodate,** $(C_3H_6N_2H_6)_3(RhCl_6)_2$; **pyridinium chlororhodate,** $(C_5H_5.NH)_3RhCl_6$; **β-picolinium chlororhodate,** $(C_5H_4.CH_3.NH)_3RhCl_6$; **lutidinium chlororhodate,** $\{C_5H_2(CH_3)_3NH\}_3RhCl_6$; **collidinium chlororhodate,** $\{C_5H_2(CH_3)_3.NH\}_3RhCl_6$; **quinolinium chlororhodate,** $(C_9H_7.NH)_3RhCl_6$; and **iso-quinolinium chlororhodate,** $(C_9H_7.NH)_3RhCl_6$. A. Gutbier also prepared **tetramethylammonium enneachlorodirhodate,** $\{(CH_3)_4N\}_3Rh_2Cl_9$; **tetraethylammonium eneachlorodirhodate,** $\{(C_2H_5)_4N\}_3Rh_2Cl_9$.

According to A. Gutbier and A. Hüttlinger, bromine begins to act on finely-divided rhodium at 250°, forming a bromide which varies in composition with the temp., presumably owing to the dissociation of **rhodium tribromide,** $RhBr_3$, in accord with the balanced reaction: $2Rh+3Br_2 \rightleftharpoons 2RhBr_3$—*vide supra*, the trichloride. G. Goloubkine prepared the tribromide by dissolving spongy rhodium in hydrobromic acid saturated with bromine:

One gram of spongy rhodium is heated with 24 grms. of 40 per cent. hydrobromic acid containing 7 grms. of bromine in a sealed tube at 80° to 100° for 48 hrs. The contents of the tube are distilled under diminished press., the residue treated with a little water, and again distilled to remove all hydrobromic acid. The bromide remaining is dissolved in water, and the soln. evaporated in vacuo over sulphuric acid, the final drying of the product being carried out in vacuo over fused potassium hydroxide. If the spongy rhodium used contains zinc or bismuth, the resulting impure bromide is reduced in a current of hydrogen; the zinc or bismuth bromide sublimes, leaving pure rhodium, from which the pure bromide is obtained by the treatment already detailed.

The *dihydrate*, $RhBr_3.2H_2O$, is very dark red, and is freely soluble in water. It gives off water and hydrogen bromide at 100° to 140°. A soln. of potassium hydroxide precipitates **rhodium dihydroxybromide,** $Rh(OH)_2Br.2H_2O$, and the filtrate yields the complex K_2RhBr_5. A series of pentabromoperrhodites has been prepared by the union of alkali and other bromides with rhodium tribromide.

S. M. Jörgensen prepared **rhodium hexamminobromide,** $[Rh(NH_3)_6]Br_3$, by treating a soln. of the corresponding chloride or nitrate with hydrobromic acid. The white, rhombic plates are stable at 100°. F. M. Jäger prepared **rhodium** ***l*****-trisethylenediaminobromide,** $[Rh\,en_3]Br_3.2H_2O$, in colourless, ditetragonal bipyramids with the axial ratio, $a:c=1:0.8330$, which are isomorphous with the corresponding cobaltic salt. E. Rosenbohm studied the magnetic susceptibility. M. Delépine and R. Charonnat obtained the dextro- and lævo-forms of this salt, and what they regarded as a compound **cobaltic rhodium trisethylenediaminobromide,** $[Co_{0.5}Rh_{0.5}\,en_3]Br_3.3H_2O$. C. J. Dippel and F. M. Jäger prepared dextro- and lævo-forms of αβδ- and ββδ-diaminopentane, **rhodium trisdiaminopentanobromide,** $[Rhptn_3Br_3].2H_2O$. P. Poulenc prepared **rhodium trispyridinotribromide,** $[Rh(C_5H_5N)_3Br_3]$; **pyridinium tetrabromobispyridinoperrhodite,** $[Rh(C_5H_5N)_2Br_4]C_5H_5N$; **rhodium dibromoquaterpyridinobromide,** $[Rh(C_5H_5N)_4Br_2]Br.6H_2O$; **pyridinium enneabromodiperrhodite acid,** $(C_5H_5N)_3H_3[Rh_2Br_9]$; and **rhodium hexabromoaquobispyridine,** $[Rh_2(C_5H_5N)_2(H_2O)Br_6].2H_2O$. F. M. Jäger and H. B. Blumendal prepared **rhodium triaminocyclopentanobromide,** $[Rh(C_5H_{12}N_2)_3]Br_3.H_2O$. By treating a soln. of aquopentamminohydroxide with hydrobromic acid, S. M. Jörgensen prepared **rhodium aquopentamminobromide,** $[Rh(NH_3)_5(H_2O)]Br_3$, in pale yellow, rhombic crystals, which lose their constitutional water at 100°. The salt is soluble in water, and the soln. gives characteristic precipitates with gold bromide, and magnesium sulphate. S. M. Jörgensen obtained **rhodium bromopentamminobromide,** $[Rh(NH_3)_5Br]Br_2$, by boiling with an excess of ammonia a soln. of the rhodium-zinc alloy in hydrobromic acid and bromine, as in the case of the corresponding chloride; and also, by heating the aquopentamminobromide at 100°, or heating it with an excess of hydrobromic acid on a water-bath. E. Birk and H. Kamm found that the bromopentamminobromide is quantitatively converted into the tribromotriammine at 210°; and at 280°, the triammine forms the monammine. The chloride and

iodides cannot be obtained by the same thermal decomposition. H. Töpsöe said that the yellow crystals are rhombic. S. M. Jörgensen observed that the salt is nearly insoluble in cold water, in hydrochloric acid, and in alcohol. It has a constitution like that of the chloropentamminochloride; and when treated with nitric acid, or silver carbonate, it forms the corresponding salts. With hydrochloric acid, it forms **rhodium bromopentamminochloride,** $[Rh(NH_3)_5Br]Cl_2$. J. N. Brönsted and A. Petersen gave 0·015 for the molal solubility of the salt at 20°. Moist silver oxide forms **rhodium bromopentamminohydroxide,** $[Rh(NH_3)_5Br]$-$(OH)_2$, which has properties similar to those of the corresponding chloropentamminohydroxide. B. E. Dixon prepared **rhodium hydroxylpentamminobromide,** $[Rh(NH_3)_5(OH)]Br_2.H_2O$. S. M. Jörgensen prepared **rhodium dichloroquaterpyridine bromide,** $[Rhpy_4Cl_2]Br$, by the action of hydrobromic acid on the chloride. E. Birk and H. Kamm found that the light brown crystals of **rhodium tribromotriamminobromide,** $[Rh(NH_3)_3Br_3]$, prepared as just indicated, are insoluble in water, acids, and alkali lye. At 280°, it forms **rhodium monamminotribromide,** $Rh(NH_3)Br_3$, soluble in conc. acids. L. Tschugaeff and W. Lebendinsky prepared **rhodium bisdimethylglyoximediamminobromide,** $[Rh(NH_3)_2D_2H_2]Br$, and the **rhodium bisdimethylglyoximediamminobromoplatinate.**

P. Poulenc prepared **sodium hexabromoperrhodite,** $Na_3[RhBr_6].12H_2O$, in red crystals which are not isomorphous with the corresponding chloride. A. Gutbier and A. Hüttlinger prepared **ammonium pentabromoperrhodite,** $(NH_4)_2RhBr_5$, by passing hydrogen bromide through a soln. of the corresponding potassium salt, and adding to the filtrate from the precipitated potassium bromide, a dil. soln. of ammonium bromide. Dark green crystals are deposited if the soln. is allowed to stand a few days. A conc. soln. of ammonium bromide does not furnish so good a crop of crystals as is the case with a dil. soln.—presumably owing to a solvent action. G. Goloubkine also prepared this salt by adding a slight excess of rhodium tribromide to a soln. of ammonium bromide, evaporating the liquid to dryness, and extracting the excess of rhodium tribromide with alcohol. A. Gutbier and A. Hüttlinger prepared **potassium pentabromoperrhodite,** K_2RhBr_5, by heating finely-divided rhodium, mixed with potassium bromide, in a current of bromine vapour. The cold mass is extracted with water, and the filtered soln. evaporated for crystallization. The crystals appear in dark green leaflets. G. Goloubkine obtained the potassium salt as in the case of the ammonium salt; and similarly with **rubidium pentabromoperrhodite,** Rb_2RhBr_5; A. Gutbier and A. Hüttlinger obtained this salt, as a dark green precipitate by adding rubidium bromide to a soln. of the potassium salt; and similarly with **cæsium pentabromoperrhodite,** Cs_2RhBr_5. G. Goloubkine prepared **sodium pentabromoperrhodite,** Na_2RhBr_5, by the method she employed for the ammonium salt; and likewise also with **barium pentabromoperrhodite,** $BaRhBr_5$. P. Poulenc prepared green, hexagonal crystals of **ammonium enneabromodiperrhodite,** $(NH_4)_3[Rh_2Br_9]$, which are isomorphous with the corresponding **potassium enneabromodiperrhodite,** $K_3[Rh_2Br_9]$; **rubidium enneabromodiperrhodite,** $Rb_3[Rh_2Br_9]$; and **cæsium enneabromodiperrhodite,** $Cs_3[Rh_2Br_9]$.

P. Poulenc obtained a salt of **rhodium tetrabromide,** namely, $Rh(C_5H_5N)_2Br_4$-(C_5H_5N).

According to G. Goloubkine, a warm, conc. soln. of potassium iodide produces a black precipitate of **rhodium triiodide,** RhI_3, when added to a soln. of rhodium tribromide. No precipitate is formed in cold, dil. soln.

A. Werner prepared **rhodium trisethylenediaminoiodide,** $[Rh\,en_3]I_3.1\frac{1}{2}H_2O$, by the action of sodium iodide on the corresponding chloride; it forms crystals which are soluble in water. F. M. Jäger said that the crystals are rhombic with the axial ratios $a:b:c=0·8541:1:0·8632$, and are isomorphous with the corresponding cobaltic salt. J. P. Mathieu studied the absorption spectrum of soln. of the salt. According to A. Werner, if the *d*-camphornitronate is treated with sodium iodide, **rhodium *d*-trisethylenediamminoiodide,** $[Rh\,en_3]I_3.1\frac{1}{2}H_2O$, is

formed in cubic crystals with $[\alpha]_D=48°$. F. M. Jäger said that the crystals of **rhodium *l*-trisethylenediaminoiodide,** $[Rh\,en_3]I_3.H_2O$, are rhombic with the axial ratios $a:b:c=0\cdot8064:1:0\cdot7380$, and isomorphous with the corresponding cobaltic salt. M. Delépine and R. Charonnat obtained what they regarded as **cobaltic rhodium trisethylendiamminoiodide,** $[Co_{0\cdot5}Rh_{0\cdot5}\,en_3]I_3.3H_2O$. A. Werner also prepared the lævo-salt. L. Tschugaeff and W. Lebendinsky prepared **rhodium bisdimethylglyoximodiamminoiodide,** $[Rh(NH_3)_2D_2H_2]I$. C. J. Dippel and F. M. Jäger, and F. M. Jäger and H. B. Blumendal prepared dextro- and lævo-forms of $\alpha\beta\delta$- and $\beta\beta\delta$-diaminopentane, **rhodium trisdiaminopentaneiodide,** $[Rhptn_3]I_3.1\frac{1}{2}H_2O$. S. M. Jörgensen prepared **rhodium iodopentamminoiodide,** $[Rh(NH_3)_5I]I_2$, by heating the aquopentamminohydroxide with an excess of hydriodic acid at 100°. H. Töpsöe said that the rhombic crystals are isomorphous with those of the chloride and bromide. They have the colour of potassium dichromate, and are soluble in cold water, but more soluble in hot water; they are insoluble in hydriodic acid, and in alcohol. If digested with dil. hydrochloric acid, a chrome-yellow **rhodium iodopentamminochloride,** $[Rh(NH_3)_5I]Cl_2$, sparingly soluble in water, insoluble in alcohol, is formed. L. Tschugaeff prepared **rhodium triiodotriammine,** $[Rh(NH_3)_3I_3]$, in small reddish-brown prisms, by warming an aq. soln. of rhodium triiodide with an excess of ammonia.

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§ 8. The Rhodium Ammines

Compounds of the tervalent rhodium salts with ammonia were observed by L. N. Vauquelin [1] in 1813, by J. J. Berzelius in 1828, by C. Claus in 1854, and by E. Frémy in 1852. Some of them have been systematically examined by S. M. Jörgensen, A. Werner, F. M. Jäger, and R. Charonnat.

I. The **hexammine family** or compounds with the tervalent basic groups $[RhA_6]^{\cdots}$.

(i) *Hexammines*, $[Rh(NH_3)_6]X_3$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) sulphate; (5) nitrate; (6) hydronitrate; (7) phosphate; and (8) sodium pyrophosphate.

(ii) *Trisethylenediammines*, $[Rhen_3]X_3$, represented by racemic, dextro-, and lævo-forms of (1) chloride; (2) bromide; (3) iodide; (4) nitrate; (5) thiocyanate; (6) chlorotartrate; and (7) camphornitronate.

(iii) *Trisdiaminopentanes*, $[Rhptn_3]X_3$, represented by the dextro- and lævo-forms of $\alpha\beta\delta$- and $\beta\beta\delta$-diaminopentanes—(1) chloride; (2) chlorate; (3) perchlorate; (4) bromide; (5) iodide; (6) sulphate; (7) nitrite; (8) nitrate; and (9) tartrate.

(iv) *Aquopentammines*, $[Rh(NH_3)_5(H_2O)]X_3$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) sulphate, and sulphatochloroplatinate; (5) nitrate and nitratochloroplatinate; (6) hydronitrate; (7) phosphate; and (8) sodium pyrophosphate.

II. The **pentammine family** or compounds with the bivalent basic group $[RhA_5X]^{\cdot\cdot}$.

(i) *Hydroxypentammines*, $[Rh(NH_3)_5(OH)]X_2$, represented by (1) the bromide; (2) the sulphate; and (3) the nitrate.

(ii) *Chloropentammines*, $[Rh(NH_3)_5Cl]X_2$, represented by (1) hydroxide; (2) chloride, and chloroplatinate; (3) sulphate; (4) hydrosulphate; (5) carbonate; (6) nitrate; and (7) fluosilicate.

(iii) *Bromopentammines*, $[Rh(NH_3)_5Br]X_2$, represented by (1) chloride; (2) bromide; (3) nitrate; and (4) carbonate.

(iv) *Iodopentammines*, $[Rh(NH_3)_5I]X_2$, represented by (1) iodide; (2) sulphate; and (3) nitrate.

(v) *Nitritopentammines*, $[Rh(NH_3)_5(NO_2)]X_2$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) sulphate; (5) hydrosulphate; and (6) nitrate.

(vi) *Nitratopentammines*, $[Rh(NH_3)_5(NO_3)]X_2$, represented by (1) chloride, and the chloroplatinate; (2) nitrate; and (3) dithionate.

III. The **tetrammine family** or compounds with the univalent basic group $[RhA_4X_2]^{\cdot}$.

(i) *Dichloroquaterpyridines*, $[Rhpy_4Cl_2]X$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) sulphate; and (5) nitrate, as well as a complex with $[Rhpy_2Cl_4]$.

(ii) *Dichloroaquotrispyridine*, $[Rhpy_3(H_2O)Cl_2]$, represented by a complex with $[Rhpy_2Cl_4]$.

(iii) *Dibromoquaterpyridine*, $[Rh(C_5H_5N)_4Br_2]Br.6H_2O$.

IV. The **triammine family**, or compounds of the null-valent group $[RhA_3X_3]$.

(i) *Trichlorotrispyridines*, $[Rhpy_3Cl_3]$.

(ii) *Tribromotrispyridines*, $[Rh(C_5H_5N)_3Br_3]$; also $[Rh_2(C_5H_5N)_2(H_2O)Br_6].2H_2O$ and $2RhBr_3.3C_5H_5N.3HBr$.

(iii) *Trichloroaquobispyridines*, $[Rhpy_2(H_2O)Cl_3]$, in its cis- and trans-forms.

V. The **diammine family** or compound of the univalent $[RhA_2X_4]'$.

(i) *Tetrachlorobispyridines*, $[Rhpy_2Cl_4]'$, represented by cis- and trans-forms of the potassium, ammonium, silver, and pyridinium salts as well as complexes with $[Rhpy_3(H_2O)Cl_2]$, and with $[Rhpy_4Cl_2]$.

(ii) *Nitratotrichlorobispyridines*, $[Rhpy_2(NO_3)Cl_3]$, represented by cis- and trans-forms of the ammonium, potassium, silver, and pyridinium salts.

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§ 9. The Rhodium Sulphides

According to J. J. Berzelius,[1] **rhodium monosulphide,** RhS, is formed when rhodium is heated in sulphur vapour; the metal takes up sulphur with incandescence. H. Debray found that crystals of the monosulphide are produced when finely-divided rhodium is heated with molten pyrite, and the regulus extracted with dil. hydrochloric acid; L. N. Vauquelin, when ammonium chloroperrhodite is heated with sulphur; L. R. von Fellenberg, by precipitating a sulphide from an aq. soln. of sodium chloroperrhodite with hydrogen sulphide, washing the precipitate with boiling water, and heating the dried product in a current of carbon dioxide. The sulphide is a grey powder, or a bluish-white, metallic-looking mass. When heated in air, L. N. Vauquelin observed that it gives off sulphur dioxide, and leaves the metal in a spongy, friable state; and L. R. von Fellenberg, that when it is heated with chlorine, sulphur and rhodium chlorides are formed. The monosulphide resists all ordinary solvents. E. Leidié could not satisfy himself that the monosulphide is a definite compound, but regarded it rather as a mixture of rhodium and rhodium hemitrisulphide formed by the partial dissociation of the latter at a high temp. V. N. Ivanoff obtained a complex with thiocarbamide resembling that with platinum.

According to R. Juza and co-workers, the following rhodium sulphides appear when the higher sulphide is heated, Rh_9S_8, Rh_3S_4, Rh_2S_3, and Rh_2S_5, but not the disulphide. Starting with the hemipentasulphide, the vap. press. at different temp. shows that the sulphide is decomposing at about 760° when the vap. press. approximates 170 mm., and at 1043°, it furnishes Rh_2S_3, which begins to decompose when the vap. press. is about 122 mm. forming Rh_3S_4. This compound breaks

down at about 1003°, when the vap. press. is about 25 mm. to form $RhS_{0.8}$ The sp. gr. is 7·51 at 25°/4°, and the mol. vol. 158. The corresponding values for **rhodium tritatetrasulphide,** Rh_3S_4, are 6·33, and 69·0; and the vap. press. *p* mm.,

	953°	1003°	1043°	1083°
p	8	24	54	120

There are two forms of **rhodium sesquisulphide,** or **rhodium hemitrisulphide,** Rh_2S_3. One form was produced in the dry way by E. Leidié, by heating the trichloride prepared at 400° in a current of dry hydrogen sulphide at a temp. not exceeding 360°, because at 400° the partial dissociation of the hydrogen sulphide forms hydrogen which reduces the rhodium sulphide to metal. For the same reason, the hydrogen sulphide employed should be free from hydrogen. Ammonium chloroperrhodite in place of rhodium trichloride gives unsatisfactory results. The black powder is crystalline and the crystals are pseudomorphs after the original trichloride. R. Juza and co-workers found that the space-lattice is formed by the coupling of two pyrite cubes; the sp. gr., 6·40 at 25°/4°; the mol. vol., 47·2; and the vap. press., *p* mm.,

	953°	1003°	1043°	1083°
p	19	56	137	300

The hemitrisulphide is stable up to about 500°. At a dull red-heat in an atm. of nitrogen, it loses 8 per cent. of sulphur, and the residue corresponds with the supposed monosulphide. If heated at bright redness in vacuo, or in a brasqued crucible, it yields a regulus which has a metallic appearance but contains 9 per cent. of sulphur. The whole of the sulphur can only be expelled in the oxy-hydrogen flame. Rhodium sesquisulphide is insoluble in alkali lye, and it is not attacked by bromine-water, nor by hydrochloric acid, nitric acid, or aqua regia. When heated strongly in air or oxygen, the oxides of sulphur and of rhodium are formed.

E. Leidié found the hemitrisulphide can be prepared by passing a current of hydrogen sulphide into a soln. of the trichloride, and then raising the temp. to 100° so as to decompose the hydrosulphide, $Rh_2S_3.3H_2S$, which is formed. Less hydrogen sulphide than is required for the precipitation is employed, for the excess of rhodium salt is precipitated from the boiling soln. by the hydrogen sulphide from the decomposition of the hydrosulphide. The black powder is insoluble in alkali sulphides, in nitric and hydrochloric acids, and in aqua regia at 100°. It is not acted on by moist air, or by bromine. E. Leidié found that this product contains rather more sulphur than corresponds with the hemitrisulphide, but when heated in vacuo at 440°, it loses sulphur dioxide and water, and has then a composition approximating Rh_2S_3.

J. J. Berzelius observed that the brown precipitate formed by ammonium sulphide in a hot soln. of sodium chloroperrhodite becomes acidic when exposed to air; it dissolves in potassium hydrosulphate and partly in potash lye. H. V. Collet-Descotils added that it forms a brown soln. with nitric acid. E. Leidié observed that a dark brown precipitate of **rhodium hydrosulphide,** $Rh_2S_3.3H_2S$, or $Rh(HS)_3$, is formed when a soln. of a rhodium salt is mixed with a large excess of hydrogen sulphide in a closed vessel. The precipitation of the rhodium is complete in a few minutes at 100°, but requires months at ordinary temp. The hydrosulphide is insoluble in alkali lye and in hydrochloric or nitric acid, but it is attacked by bromine-water and aqua regia. When heated with 500 times its weight of water in a closed vessel or in an atm. of nitrogen, the hydrosulphide is decomposed into rhodium sulphide and hydrogen sulphide. Whenever a rhodium salt is precipitated by hydrogen sulphide at 100°, the hydrosulphide is formed, but it immediately decomposes, the change taking place more readily in presence of an excess of rhodium salt than in presence of water alone. H. Baubigny said that the hydrosulphide is stable in the presence of an excess of hydrogen sulphide. L. de

Boisbaudran reported that the hemitrisulphide formed at a low temp. is soluble in ammonium sulphide, and hydrochloric acid, but his " sulphide " may have been a mixture of sulphide and oxide.

According to E. Leidié, if a normal salt of rhodium, such as an alkali chloroperrhodite, is treated with an excess of a conc. soln. of an alkali monosulphide, a compound of rhodium sulphide with the alkali sulphide is precipitated, and is stable in presence of excess of the latter, but is decomposed by water. When the liquid contains not more than 16 mols. of water to each mol. of sodium sulphide the precipitate has the composition of **sodium sulphoperrhodite,** $3Na_2S.Rh_2S_3$, or Na_3RhS_3. With 1·10 mols. of water to each mol. of sodium sulphide, the precipitate is rhodium sulphide alone, and between these limits the double sulphide is gradually dissociated as the proportion of water increases. With 550 mols. of water to each mol. of sodium sulphide, the precipitate formed in the cold is yellow rhodium hydroxide, the alkaline sulphide being completely dissociated by the water into the hydroxide and hydrogen sulphide. E. Leidié obtained **potassium sulphoperrhodite,** $3K_2S.Rh_2S_3$, or K_3RhS_3, in a similar manner.

L. Thomassen prepared **rhodium disulphide,** RhS_2, by melting the components in an evacuated quartz tube, and slowly cooling the product during 74 hrs. from 900° to 430°, and during 34 hrs. to ordinary temp. The product is a greyish-black, coarse powder with some sintered clumps. About 7 per cent. of the sulphur is not taken up by the rhodium. The X-radiogram shows that the disulphide crystals belong to the cubic system, and have the pyritic structure, with the parameter *a*, 5·574 A. P. Niggli, and L. Pauling and M. L. Huggins discussed the subject. L. Wöhler and co-workers prepared **rhodium hemipentasulphide,** Rh_2S_5 by the action of sulphur on rhodium trichloride at 600°. H. G. Krall said that the hemipentasulphide is a dark grey crystalline mass, which is not attacked by dil. or conc. mineral acids, or aqua regia. R. Juza and co-workers found that the space-lattice is formed by the coupling of two pyrite cubes; the sp. gr., 5·00 at 25°/4°; the mol. vol., 73·0; and the vap. press., *p* mm.,

	715°	757°	798°	830°
p	40	122	285	575

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§ 10. The Rhodium Sulphates

J. J. Berzelius[1] prepared **rhodium sulphate,** $Rh_2(SO_4)_3$, by heating the hemitrisulphide with fuming nitric acid, or with bromine-water; H. St. C. Deville and H. Debray, by heating the metal at a red-heat with molten potassium hydrosulphate, or by the action of boiling, conc. sulphuric acid on an alloy of rhodium and lead; and E. Leidié, by the action of conc. sulphuric acid on rhodium trichloride, or a double chloride. The soln. is evaporated to a syrupy consistency, and, as recom-

mended by C. Claus, and E. Leidié, finally heated to a constant weight at 440° so as to remove the whole of the free acid. The sulphate begins to decompose at 500°, and it forms the hemitrioxide in air at a red-heat. J. J. Berzelius thought that **rhodious sulphate,** $RhSO_4$, is formed, and he added that the same salt is formed when rhodium hemitrisulphide is roasted in air—these statements have not been confirmed. The deliquescent sulphates described by J. J. Berzelius, and C. Claus probably contained an excess of acid. Rhodium sulphate, $Rh_2(SO_4)_3$, forms a brick-red, non-hygroscopic powder, stable in presence of water if the latter does not exceed 16 eq. per eq. of salt, but decomposed by a larger quantity with formation of a basic sulphate and free sulphuric acid. When boiled with large quantities of water until the washings are no longer acid, it yields **rhodium oxysulphate,** $Rh_2O_3.Rh_2(SO_4)_3$, as a lemon-yellow, insoluble powder. When a soln. of the normal sulphate is treated with alkali hydroxide or carbonate, the hydrated hemitrioxide is precipitated; aq. ammonia in the cold precipitates a basic salt, and with boiling soln., the hydrated hemitrioxide—the presence of an excess of an ammonium salt retards the precipitation.

S. M. Jörgensen prepared **rhodium hexamminosulphate,** $[Rh(NH_3)_6]_2(SO_4)_3.3H_2O$, by adding alcohol to the soln. of the hydroxide in sulphuric acid. For some reactions, *vide infra*, the hexamminonitrate. S. M. Jörgensen also obtained **rhodium aquopentamminosulphate,** $[Rh(NH_3)_5(H_2O)]_2(SO_4)_3.3H_2O$, by adding alcohol to a soln. of the corresponding hydroxide in sulphuric acid. The yellowish-green prisms are isomorphous with the corresponding cobaltic salt. This compound is sparingly soluble in cold water, but freely soluble in hot water; and when it is heated to 100°, it is partially transformed into the hexammine. If the soln. be treated with platinic chloride, there is formed **rhodium aquopentamminosulphato-chloroplatinate,** $[Rh(NH_3)_5(H_2O)]_2(SO_4)_2(PtCl_6)$. S. M. Jörgensen prepared **rhodium chloropentamminosulphate,** $[Rh(NH_3)_5Cl](SO_4).2H_2O$, by cooling a hot soln. of the hydrate in dil. sulphuric acid. The yellow prisms are sparingly soluble in cold water, but readily soluble in boiling water. If the corresponding chloride be treated with conc. sulphuric acid, and cooled, sulphur-yellow crystals of **rhodium chloropentamminohydrosulphate,** $4[Rh(NH_3)_5Cl](SO_4).3H_2SO_4$, are formed, sparingly soluble in cold water, but more soluble in hot water. S. M. Jörgensen reported **rhodium iodopentamminosulphate,** $[Rh(NH_3)_5I](SO_4).3H_2O$, to be formed by the spontaneous evaporation of a soln. of the corresponding chloride in conc. sulphuric acid. The *trihydrate* becomes anhydrous at 100°; and the anhydrous salt is precipitated by adding alcohol to the mother-liquor from the trihydrate. B. E. Dixon prepared **rhodium hydroxylpentamminosulphate,** $[Rh(NH_3)_5(OH)]_2SO_4.2H_2O$. S. M. Jörgensen prepared **rhodium nitritopentamminosulphate,** $[Rh(NH_3)_5(NO_2)]SO_4$, as well as **rhodium nitritopentamminohydrosulphate,** $2[Rh(NH_3)_4(NO_2)]SO_4.3H_2SO_4$. S. M. Jörgensen also obtained **rhodium dichlorotetrapyridinosulphate,** $[Rhpy_4Cl_2]_2SO_4$. F. M. Jäger and H. B. Blumendal prepared **rhodium trisaminocyclopentanosulphate,** $[Rh(C_5H_{12}N_2)_3]_2(SO_4)_3$.

F. Krauss and H. Umbach dissolved rhodic hydroxide precipitated in the cold, in dil. sulphuric acid, evaporated the liquid over conc. sulphuric acid, and added ether. Yellow, **rhodic sulphate,** $Rh_2(SO_4)_3.15H_2O$, was precipitated. Three of the mols. of water in the *pentadecahydrate* are zeolitically combined, and possibly also some of the other mols. of water. The aq. soln. gives the normal reactions, and on evaporation yields a red *tetrahydrate*, $Rh_2(SO_4)_3.4H_2O$, where the water is zeolitically combined. Freshly-prepared soln. do not react in this manner. If a conc. soln. of the double salt with cæsium is mixed with one-third its vol. of conc. sulphuric acid, and evaporated, a yellow, crystalline powder of **rhodic hydrosulphate,** $Rh_2(SO_4)_3.H_2SO_4.16H_2O$, is formed. R. Bunsen, and K. Seubert and K. Kobbé, prepared **sodium rhodium disulphate,** $Na_2SO_4.Rh_2(SO_4)_3$, or $NaRh(SO_4)_2$, by heating the double sulphate with conc. sulphuric acid, but they could not obtain it with water of crystallization. A. Piccini and

L. Marino prepared a series of **rhodium alums** by allowing a mixed soln. of the two sulphates to crystallize. The soln. should contain about two-thirds of the theoretical quantity of alkali sulphate, and an excess of sulphuric acid. The soln. should be kept at a low temp. For example, J. J. Berzelius described potassium rhodium sulphate, $K_2SO_4.Rh_2(SO_4)_3.nH_2O$, and A. Piccini and L. Marino showed that **potassium rhodium disulphate,** or *potassium rhodium alum*, $K_2SO_4.Rh_2(SO_4)_3.24H_2O$, or $KRh(SO_4)_2.12H_2O$, can be obtained in the crystalline state only by allowing the soln. to stand for a long time at a temp. not exceeding 5°; at a higher temp., an uncrystallizable, syrupy liquid is formed. The crystals are brownish-yellow and belong to the cubic system. They are stable in air, and freely soluble in water. The corresponding **rubidium rhodium disulphate,** *rubidium rhodium alum*, $RbRh(SO_4)_2.12H_2O$, likewise furnishes honey-yellow, octahedral crystals which exhibit no cleavage. Their indices of refraction are 1·4977 for red-light, 1·5004 for yellow-light, and 1·5036 for green-light. The crystals melt at 108° to 109° to form a red liquid. The easiest salt of the series to prepare is **cæsium rhodium disulphide,** or *cæsium rhodium alum*, $CsRh(SO_4)_2.12H_2O$, because it is the least soluble in cold water. It furnishes honey-yellow, octahedral crystals with no cleavage, and with the indices of refraction 1·5063 for red-light, 1·5077 for yellow-light, 1·5112 for green-light, and 1·5184 for violet-light. F. Krauss and H. Umbach found that the orange cubic crystals of the *dodecahydrate* of cæsium alum have the lattice constant a=12·30 A. The sp. gr. is 2·238 at 20°/4°. If dried below 100°, a yellow *hexahydrate* of sp. gr. 2·720, and a brown, sparingly-soluble *dihydrate* of sp. gr. 3·078, are formed. When the dihydrate is heated above 100°, it decomposes; but if it be heated with conc. sulphuric acid, the anhydrous salt is formed as a slightly-soluble, rose-coloured powder of sp. gr. 3·29 at 20°/4°. According to A. Piccini and L. Marino, the dodecahydrate melts at 110° to 111° to form a yellowish-red liquid; and when warmed in a desiccator, it loses water, retaining its yellow colour up to 100°, it becomes yellowish-red at 150° to 180°, and brown at about 250° when it is almost anhydrous, and it is still quite soluble in water. Rhodium can be separated from iridium by evaporating an acidic soln. of the sulphates mixed with cæsium sulphate, when the cæsium rhodium alum crystallizes from the liquid, and by recrystallization it can be obtained quite free from iridium. F. Krauss and H. Umbach evaporated a soln. of the cæsium alum on a water-bath, and obtained a dark yellow powder of the *tetrahydrate*, $CsRh(SO_4)_2.4H_2O$, which loses water continuously when heated, and does not liberate sulphate-ions in cold, dil. aq. soln., but the complex breaks down gradually when heated. At 165°, the tetrahydrate forms a dihydrate of sp. gr. 3·4 at 20°/4°. According to A. Piccini and L. Marino, orange-yellow crystals of **ammonium rhodium disulphate,** or *ammonium rhodium alum*, $(NH_4)Rh(SO_4)_2.12H_2O$, are less soluble in water than is the case with the potassium salt. The orange-yellow crystals exhibit no cleavage, and their indices of refraction are 1·5073 for red-light, 1·5103 for yellow-light, and 1·5150 for green-light. The crystals are stable in air, and melt at 102° to 103° to a brownish-red liquid. After heating to redness, rhodium contaminated with sulphate remains as a residue. The sulphate is not completely removed by reheating the rhodium with ammonium carbonate. The crystals of **thallous rhodium disulphate,** or *thallous rhodium alum*, $TlRh(SO_4)_2.12H_2O$, were difficult to prepare on account of the low solubility of thallous sulphate. The crystals exhibit no cleavage, and the indices of refraction are 1·5458 for red-light, 1·5480 for yellow-light, and 1·5490 for green-light. The alum is soluble in water, and on exposure to air for a long time, the alum acquires a white, pulverulent film. E. Leidié said that normal rhodium sulphate forms neither double salts nor alums.

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§ 11. The Carbonates, Nitrates, and Phosphates of Rhodium

Normal **rhodium carbonate** has not been prepared, but S. M. Jörgensen[1] obtained **rhodium chloropentamminocarbonate,** $[Rh(NH_3)_5Cl]CO_3.H_2O$, by triturating the corresponding chloride with silver carbonate and water, and treating the filtrate with alcohol. The pale yellow, crystalline powder is soluble in water, and it is decomposed by acids forming the corresponding salt. S. M. Jörgensen also prepared **rhodium bromopentamminocarbonate,** $[Rh(NH_3)_5Br]CO_3,nH_2O$, in a similar manner.

According to W. H. Wollaston, a soln. of hydrated rhodium hemitrioxide in nitric acid is red, and uncrystallizable; J. J. Berzelius concentrated the yellow liquid to a syrup; and E. Leidié obtained a deep yellow, hygroscopic **rhodium trinitrate,** $Rh(NO_3)_3.2H_2O$, which is readily soluble in water, but not in alcohol.

S. M. Jörgensen prepared **rhodium hexamminonitrate,** $[Rh(NH_3)_6](NO_3)_3$, by adding nitric acid to a hydrochloric acid soln. of sodium rhodium hexamminopyrophosphate, when **rhodium hexamminohydronitrate,** $[Rh(NH_3)_6](NO_3)_3.HNO_3$, is precipitated in colourless needles. The acid salt reverts to the normal nitrate when it is treated with alcohol, or washed with water. The white powder consists of small rhombic plates. It can be recrystallized by cooling the soln. in hot water; it is sparingly soluble in water—1 part of salt dissolves in 48 to 49 parts of cold water—it is almost insoluble in nitric acid; and when repeatedly evaporated with hydrochloric acid, it forms the hexamminochloride. With a cold, sat. aq. soln. of the nitrate, dil. nitric acid gives a precipitate of the unchanged salt; conc. hydrochloric acid precipitates the chloride; 1 : 1 dil. hydrobromic acid precipitates the bromide; potassium iodide gives a pale yellow precipitate; dil. sulphuric acid gives no precipitate; hydrofluosilicic acid gives a white precipitate; hydrochloroplatinic acid, a pale brown precipitate; potassium chloroplatinite, a pale brown precipitate; hydrochloroauric acid, a straw-yellow precipitate; mercuric chloride, no precipitate, and in acid soln., a white precipitate; sodium chloromercuriate, a white precipitate; sodium phosphate, no precipitate unless ammonia is also added; sodium pyrophosphate, a white precipitate; sodium dithionate, a white precipitate soluble in excess; potassium chromate, a lemon-yellow precipitate; potassium dichromate, an orange-yellow precipitate; potassium permanganate, a violet-red precipitate; iodine in potassium iodide, a greyish-green precipitate; ammonium oxalate, no precipitate unless ammonia is also added when precipitation is complete; potassium ferrocyanide, a white precipitate; potassium ferricyanide, an orange-yellow precipitate; and potassium cyanide, a white precipitate.

F. M. Jäger prepared the racemic, and lævo-forms of **rhodium trisethylenediaminonitrate,** $[Rhen_3](NO_3)_3$. The racemic form is isomorphous with the corresponding cobaltic salt, and the rhombic bipyramids have the axial ratios $a : b : c = 0{\cdot}7874 : 1 : 0{\cdot}5606$; and the lævo-salt, $a : b : c = 0{\cdot}8642 : 1 : 0{\cdot}6049$. C. J. Dippel and F. M. Jäger prepared the dextro- and lævo-forms of $\alpha\beta\delta$- and $\beta\beta\delta$-diaminopentane, **rhodium trisdiaminopentanonitrate,** $[Rhptn_3](NO_3)_3.1\frac{1}{2}H_2O$; and L. Tschugaeff and W. Lebendinsky, **rhodium bisdimethylglyoximediamminonitrate,** $[Rh(NH_3)_2D_2H_2]NO_3$. S. M. Jörgensen obtained **rhodium aquopentamminonitrate,** $[Rh(NH_3)_5(H_2O)](NO_3)_3$, by exactly neutralizing the corresponding hydroxide with nitric acid, and washing the yellow precipitate with alcohol, and dil. nitric acid. The quadratic prisms are non-efflorescent; readily soluble in water; and lose water at 100° to form the nitratopentamminonitrate. An excess

of nitric acid converts the neutral nitrate into **rhodium aquopentamminohydronitrate,** $[Rh(NH_3)_5(H_2O)](NO_3)_3.HNO_3$, in colourless crystals partly decomposed by water or by alcohol. When platinic chloride is added to a soln. of the normal nitrate, there is precipitated orange-yellow, crystalline **rhodium aquopentamminonitratochloroplatinate,** $[Rh(NH_3)_5(H_2O)](NO_3)(PtCl_6).H_2O$. This salt loses a mol. of water at 100°, and the other mol. of water is given off more slowly with the formation of nitratopentamminochloroplatinate; hydrochloric acid converts it into a soln. of hydrochloroplatinic acid, and rhodium nitratopentamminochloride.

S. M. Jörgensen prepared **rhodium chloropentamminonitrate,** $[Rh(NH_3)_5Cl](NO_3)_2$, as a yellow precipitate by treating a conc. soln. of the corresponding chloride with cold nitric acid. The crystalline precipitate is slowly formed, and it is washed with dil. nitric acid, then with alcohol, and dried in air. He also obtained the corresponding **rhodium bromopentamminonitrate,** $[Rh(NH_3)_5Br](NO_3)_2$; and **rhodium iodopentamminonitrate,** $[Rh(NH_3)_5I](NO_3)_2$. S. M. Jörgensen obtained rhodium nitratopentamminonitrate, $[Rh(NH_3)_5(NO_3)](NO_3)_2$, by heating the aquopentamminonitrate to 100°, or by treating a hot, aq. soln. of that salt with an equal vol. of conc. nitric acid. The cooling soln. deposits greenish-yellow crystals which explode when heated over a small flame. The salt is sparingly soluble in water, and insoluble in alcohol. When the aq. soln. is boiled a long time it forms the aquopentamminonitrate. The soln. gives characteristic precipitates with mercuric chloride, potassium dichromate, platinic chloride, etc. If a soln. of the nitratopentamminonitrate is dropped into a 3 : 1-soln. of hydrochloric acid, at 0°, there is formed a pale greenish-yellow precipitate of **rhodium nitratopentamminochloride,** $[Rh(NH_3)_5(NO_3)]Cl_2$; **rhodium nitratopentamminochloroplatinate,** $[Rh(NH_3)_5(NO_3)]PtCl_2$, has been prepared—*vide supra.* A corresponding **rhodium nitratopentamminodithionate,** $[Rh(NH_3)_5(NO_3)]S_2O_6.H_2O$, has been obtained, as a white, insoluble precipitate on adding a sat. soln. of the corresponding nitrate to a soln. of sodium dithionate. J. A. Christiansen and R. W. Asmussen examined the magnetic properties of **rhodium aquopentamminonitrate,** $[Rh(NH_3)_5(H_2O)]NO_3$; and J. B. Dixon prepared **rhodium hydroxylpentamminonitrate,** $[Rh(NH_3)_5(OH](NO_3)_2$. V. V. Lebedinsky and co-workers prepared **rhodium dichlorotetramminonitrate,** $[Rh(NH_3)_4Cl_2]NO_3$; and a complex with **rhodium hexathiocarbamidochlorodinitrate,** $[Rh\{CS(NH_2)_2\}_6]Cl(NO_3)_2$.

S. M. Jörgensen prepared **rhodium dichloroquaterpyridinonitrate,** $[Rhpy_4Cl_2)(NO_3)$, by adding a soln. of the corresponding chloride to dil. nitric acid. M. Delépine prepared **rhodium nitratotrichloropyridine,** $[Rhpy_2(NO_3)Cl_3]'$, in its cis- and trans-forms, represented by ammonium, potassium, silver, and pyridinium salts.

J. J. Berzelius reported a **sodium rhodium nitrate** to be formed in dark red crystals from a soln. of rhodium and sodium nitrates. The double salt is freely soluble in water, and insoluble in alcohol. A. Lancien also prepared **uranyl rhodium nitrate,** $UO_2(NO_3)_2.Rh(NO_3)_3.6H_2O$, in orange leaflets which lose half their water of crystallization in vacuo.

E. Leidié found that if a sat. soln. of ammonium chloride is added to a conc. soln. of ammonium rhodium chloride containing a considerable proportion of free nitric acid, crystalline plates resembling chromic chloride are deposited. When these are dried in vacuo, they correspond with **ammonium rhodium chloronitrate,** $RhCl_3.3NH_4Cl.NH_4NO_3$. If treated with water, they decompose into the double chloride, $Rh_2Cl_6.6NH_4Cl+3H_2O$, rhodium chloride, and gaseous products similar to those produced by the action of aqua regia on ammonium chloride. The feeble solubility of this compound must be borne in mind when ammonium chloride is employed to separate rhodium from platinum. O. E. Zwjaginstseff and co-workers said that the salt forms hexagonal crystals, that conductivity measurements show that it furnishes five ions, and that it has the formula $(NH_4)_3[RhCl_5(NH_4Cl)]NO_3$, or $[(NH_4)_3(NO_3)RhCl_6]NH_4$. O. E. Zwjaginstseff found that an aq. soln. of the pale lilac salt is blood-red, and with silver nitrate it gives an amorphous, pale rose precipitate of **ammonium silver rhodium chloronitrate,** $Ag_3[RhCl_6]NH_4NO_3$,

which is soluble in aq. ammonia, and is slightly decomposed when warmed. He also obtained **ammonium lead rhodiumchloronitrate,** $Pb_3(RhCl_6)_2.2NH_4NO_3$; and **ammonium mercury rhodium chloronitrate.** A. Lancien obtained **rhodium uranyl nitrate,** $2UO_2(NO_3)_2.Rh(NO_3)_3.5H_2O$, in orange leaflets which lose half their water in vacuo.

According to N. W. Fischer, **rhodium phosphate** is formed by boiling finely-divided rhodium with a conc. soln. of phosphoric acid, or by fusing the pulverulent rhodium with hydrated phosphoric acid at a temp. below redness. Microcosmic salt is a less energetic solvent. The dil. soln. is yellow, the conc. soln. is brown. Alkali lye produces no precipitate, but after a prolonged digestion, gelatinous hydrated rhodium hemitrioxide separates out. Aq. ammonia behaves similarly, but the colour of the soln. becomes green or blue according to the acidity of the liquid. The action is accelerated by gentle heat, but if the liquid be rapidly raised to its b.p., the change of colour does not occur. The green colour is not destroyed by boiling the liquor; nitric acid changes the blue or green colour to violet; hydrochloric acid behaves similarly in hot soln., but at a higher temp., the liquid regains its yellow colour. According to C. Claus, hydrated rhodium hemitrioxide and phosphoric acid yield **rhodium oxyphosphate,** $4Rh_2O_3.3P_2O_5.32H_2O$, sparingly soluble in acids, and in alkali lyes. The acidic mother-liquid, on evaporation, furnishes **rhodium hydrophosphate,** $Rh_2O_3.2P_2O_5.6H_2O$. A basic phosphate is deposited when a soln. of rhodium trichloride is treated with normal sodium phosphate.

S. M. Jörgensen prepared **rhodium hexamminophosphate,** $[Rh(NH_3)_6](PO_4).4H_2O$, by adding sodium phosphate to a soln. of a hexammine in the presence of an excess of ammonia. The acicular crystals are efflorescent. Soln. of an aquopentammine with dil. phosphoric acid furnish **rhodium aquopentamminophosphate,** $[Rh(NH_3)_5(H_2O)]_2(HPO_4)_3.4H_2O$, which is incompletely dehydrated at 100°. If sodium pyrophosphate is employed as precipitant with a soln. of the hexammine, **sodium rhodium hexamminopyrophosphate,** $2[Rh(NH_3)_6](NaP_2O_7).23H_2O$, is formed in white, hexagonal prisms almost insoluble in water, and insoluble in aq. ammonia. Similarly, with soln. of the aquopentammines, **sodium rhodium aquopentamminopyrophosphate,** $[Rh(NH_3)_5(H_2O)]_2(NaP_2O_7).23H_2O$, is formed. The white crystals are sparingly soluble in cold water.

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CHAPTER LXXI

PALLADIUM

§ 1. The Occurrence of Palladium

THE history of palladium is discussed in connection with platinum—*vide infra.* Octahedral, cubic crystals of palladium were reported by A. von Humboldt,[1] G. Rose, and W. H. Wollaston to occur native in Minas Geraes, Brazil; by J. D. Dana, in St. Domingo, Antilles; and by F. A. Genth, in the Urals. There is another form of palladium reported to occur in hexagonal crystals at Tilkerode, Hartz. Hence, G. Rose could discuss *die Dimorphie des Palladiums.* The hexagonal, dimorphous form was announced by J. C. L. Zincken, and he assumed that it contained selenium, and hence called it *Selenpalladium*, but later on, he told J. J. Berzelius that it was not a selenide of palladium. In a later description of the Tilkerode minerals, J. C. L. Zincken described a silvery white mineral containing palladium, silver, gold, and selenium—possibly present as admixed lead selenide—and he called it *eugenesite;* but he did not mention the relation of this mineral to his previously-described *selenpalladium.* F. Wrede found platinum is contained in selenpalladium, and J. C. L. Zincken, silver, gold, and selenium which C. F. Rammelsberg assumed to be present as clausthalite, or lead selenide. J. D. Dana called the Selenopalladium **allopalladium.** O. Luedecke also said that it occurs at Zorge, Hartz. The individuality of allopalladium has been admitted by faith, without the presentation of an accredited passport. A. Cissarz assumed that it is an amalgam.

L. J. Spencer also discussed the warranty for admitting allopalladium as a dimorphous variety of palladium, and found the evidence to be singularly "inadequate and unconvincing." In spite of the lapse of nearly a century, J. C. L. Zincken's report has not been confirmed, and L. J. Spencer therefore concluded that the original selenpalladium, or allopalladium, from the Hartz "is probably ordinary cubic palladium; the supposed hexagonal modification of palladium probably having no existence." The mineral **braggite,** (Pt, Pd, Ni)S, described in connection with platinum monosulphide, contains about 20 per cent. of palladium. J. B. Harrison reported an occurrence of palladium-rhodium alloy in the bed of the Potaro river, British Guiana, and L. J. Spencer at first thought that the mineral was allopalladium, but he later showed that it is really another mineral, **potarite,** approximately PdHg. According to A. Cissarz, the X-radiogram of allopalladium is different from those of palladium, and of potarite. Allopalladium is considered to be a palladium amalgam, poor in mercury, and to contain all the platinum metals. *Clausthalite* also contains some mercury, palladium, and several of the platinum metals with the exception of rhodium; it also contains copper, silver, zinc, nickel, and cobalt.

H. R. Adam reported a mineral from the Potgieterstrust district, South Africa, which occurs in grains showing crystal facets. It is white with a yellowish-pink tinge. It belongs to the cubic system, and is softer than sperrylite. The analysis corresponds with palladium tritantimonide, Pd_3Sb, and it has been called **stibiopalladinite.** J. Cloud, and P. N. Johnson and W. A. Lampadius described the occurrence of a *palladium gold* in the *oro polvo* from the vicinity of Porpez, or Pompeo, an old mining settlement near Sabara, Brazil. Samples from Jacutinga

and Condona contained 5 to 6 per cent. of palladium; and, according to W. H. Seamon, a specimen from Taguaril, Minas Geraes, contained: gold 91·06, palladium 8·21, and traces of silver and iron; J. J. Berzelius gave: gold 85·98, palladium 9·85, and silver 4·17; and W. J. Cock found 6 to 7 per cent. of palladium. J. Fröbel called the mineral **porpezite**—which J. D. Dana suggested is a corruption of Pompeo.

J. J. Berzelius,[2] G. Osmann, H. St. C. Deville and H. Debray, M. von Kokscharoff, S. Kern, and C. Claus reported the presence of 0·28 to 1·30 per cent. of palladium in Russian platinum ores. N. Wissotsky, and L. Duparc and M. Tikanowitch noted with samples of Russian platinum 0·15 to 0·51 per cent. of palladium in that from Tagil; 0·21 to 0·77 per cent. in that from the water-shed of the river Iss-Swetli-Bor, and Wéressowy-Ouwal; 0·18 to 0·37 per cent. in that from Kamenouchky, Koswinsky, Kanjakowsky, Omountnaïa, and Daneskin-Kamen; 0·90 to 1·36 per cent. in that from Goussewi-Kamen, Kiedrowka, Barantscha, and Solwa; 0·99 to 1·28 per cent. in that from Goussewka, Schocimika, and Obleiskaya-Kamenka. I. Koifmann noted 0·18 to 0·32 per cent. in some samples of Russian platinum ore. L. F. Svanberg, and H. St. C. Deville and H. Debray reported 0·35 to 1·66 per cent. of palladium in platinum from Choco, Colombia; E. Hussak, in Brazil; H. St. C. Deville and H. Debray, F. A. Genth, F. Weil, and A. Kromæyer, 0·60 to 1·95 per cent., in platinum from California; H. St. C. Deville and H. Debray, 0·15 per cent. in platinum from Oregon; T. T. Read described the palladium in Wyoming, U.S.A.; P. Collier, 3·10 per cent. in platinum from Plattsburg, New York; G. C. Hoffmann, 0·09 to 0·26 per cent. in platinum from British Columbia; 0·85 per cent. Spain; 1·05 to 1·80 per cent. in platinum from Australia; S. Bleckrode, 1·41 per cent. in platinum from Borneo. R. C. Wells reported up to 0·2 per cent. of palladium with a trace of platinum in the plumbojarosite of Goodsprings, Nevada, described by A. Knopf. W. C. Knight, J. F. Kemp, S. F. Emmons, and T. T. Read described the covellite occurring in the diorite ores of the Rambler Mine, Wyoming, and which contains both platinum and palladium. The mattes obtained in working the copper-nickel sulphide ores of Sudbury, Ontario, contain about 0·0068 oz. per ton of platinum metals; and the residue, after removing the copper by leaching and, according to C. Langer and C. Johnson, the nickel by Mond process, contained 1·85 per cent. Pt; 1·91, Pd; 0·56, Au; 0·39, Ir, Rh, and Ru; and Ag, 15·42. J. J. O'Neill and H. C. Gunning, and T. L. Tanton discussed the deposit at Shebandowan Lake, Canada. P. A. Wagner reported that the platinum from Merensky approximated Pt, 66 to 77 per cent.; Pd, 11 to 25 per cent.; other platinum metals, 1 to 7 per cent.; and gold, 2 to 5 per cent. H. Rössler reported platinum and palladium in silver bullion; A. Eilers, in blister copper; A. Cissarz, in Mansfeld copper shale; and P. Krusch, in graywacke.

The general occurrence of palladium was discussed in connection with the platinum metals. F. W. Clarke and H. Washington's[3] estimate for the proportion of palladium in the igneous rocks of the earth's crust is of the order $n \times 10^{11}$; I. and W. Noddack estimated $8{\cdot}5 \times 10^{-13}$ in the earth's crust; $1{\cdot}9 \times 10^{-5}$ in meteoric iron; and $4{\cdot}5 \times 10^{-6}$ in troilite; later, they gave $1{\cdot}2 \times 10^{-8}$ for the earth's crust, and 7×10^{-6} for meteorites. The subject was discussed by P. Niggli, F. Bernauer, P. Vinassa, and V. M. Goldschmidt and C. Peters. The atomic distribution of palladium, oxygen unity, is $4{\cdot}6 \times 10^{-6}$. G. Trottorelli reported 0·77 per cent. of palladium in a meteorite which fell at Collescipoli; and G. P. Merrill, and J. C. H. Mingaye reported palladium in other meteorites—*vide supra*, meteoric iron. H. A. Rowland included palladium in the list of elements having some spectral lines corresponding with some of those in the solar spectrum; J. N. Lockyer reported its presence in the sun's photosphere; and H. von Klüber said that 21 lines in the solar spectrum have been identified in the lines of palladium. V. M. Goldschmidt and C. Peters discussed the occurrence of palladium in coal.

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§ 2. The Extraction and Preparation of Palladium

According to E. Wichers and co-workers,[1] palladium recovered in the refining of copper or nickel may contain silver, gold, and platinum, as well as copper and nickel, and smaller amounts of tellurium, selenium, antimony, bismuth, lead, and

iron. Palladium recovered in the refining of crude platinum may contain small amounts of all the platinum metals, silver, gold, and base metals, such as copper, iron, lead, and zinc. W. H. Wollaston, and L. N. Vauquelin separated palladium from the soln. of the platinum metals after precipitating the platinum with ammonium chloride, by reduction with iron, or zinc, and washing with dil. nitric acid. When digested with hydrochloric acid and potassium nitrate, a soln. containing chiefly rhodium and palladium is obtained; and when evaporated it deposits crystals of potassium palladium chloride which can be separated mechanically from the other crystals, converted by potassium hydroxide into palladium oxide, and ignited for palladium. L. N. Vauquelin also precipitated the palladium as palladous diamminochloride; W. H. Wollaston, F. Döbereiner and F. Weiss, F. Krause and H. Deneke, C. Claus, and J. J. Berzelius precipitated the palladium as cyanide by adding mercuric cyanide; and R. Bunsen, as palladous iodide by adding potassium iodide, or, according to N. A. Orloff, by adding freshly-precipitated silver iodide.

P. N. Johnson and W. A. Lampadius, and W. J. Cock extracted palladium from palladium-gold ore, by fusing it with potassium nitrate and silver so that the gold amounts to about one-fourth of the whole mixture. The alloy is granulated, and then digested with dil. nitric acid. Gold remains as a residue, and silver, palladium, and copper pass into soln. The silver is precipitated as chloride, and the palladium and copper are precipitated as a black powder by treating the acidic soln. with zinc. The black powder is dissolved in nitric acid, and the soln. supersaturated with ammonia. If this soln. be treated with a slight excess of hydrochloric acid, yellow palladous diamminochloride is precipitated, can then be washed with cold water, and ignited for palladium. The hydrochloric acid soln. deposits any remaining palladium and copper when it is treated with iron. According to M. A. Mosher, palladium can also be recovered from the anode mud of copper refining plants. E. Wichers and co-workers, and R. Gilchrist and co-workers recommended the dichlorodiammine precipitation, and the following procedure:

The crude palladium, if not in soln., can be dissolved in aqua regia—300 to 350 vols. of hydrochloric acid of sp. gr. 1·18, 75 to 100 vols. of water, and 60 to 70 vols. of nitric acid of sp. gr. 1·42—in a covered porcelain dish to prevent loss as spray. Palladium oxide, if present, dissolves very slowly in aqua regia, and may therefore occur in the undissolved residue. The soln. is evaporated on the steam-bath to remove most of the excess acid, and the syrupy liquor dissolved in water and a little hydrochloric acid. The soln. of palladous chloride so obtained is diluted so as to contain 40 to 50 grms. of palladium per litre. If much silver is present, most of it will settle out as silver chloride, the remainder being kept in soln. Inasmuch as the process of purification involves a conc. chloride soln. and an ammoniacal soln. alternately, several reprecipitations may be necessary to eliminate all of the silver. After filtering off the silver chloride and other insoluble material, ammonium hydroxide is added to the soln. until no further precipitation of the flesh-coloured compound $[Pd(NH_3)_4]Cl_2.PdCl_2$ occurs. The soln. is then heated on the steam-bath for 15 to 20 mins. to redissolve the precipitate. It may be necessary to add a little more ammonium hydroxide, but an excess of this reagent is to be avoided because of the heating which results when the soln. is subsequently acidified with hydrochloric acid. Iron and certain other impurities will be precipitated as hydroxides or basic salts. The colour of the ammoniacal soln. furnishes an indication of the amount of copper that may be present. If the soln. is pale yellow or straw-coloured, very little if any copper is present. If it is blue or bluish-green, the amount of copper may be considerable and the number of reprecipitations necessary to remove all of it will be increased accordingly. If much copper is present, it may possibly be desirable to precipitate the palladium first as ammonium chloropalladate. It is probable that copper is more rapidly eliminated in this way than by the repeated precipitation of the dichlorodiammine, but the platinum metals are much more rapidly eliminated by the latter method.

If a large excess of ammonia has been added inadvertently, some of it may be removed by heating on the steam-bath for a time. The soln. is then cooled and acidified with hydrochloric acid, which causes the conversion of the soluble tetramminodichloride, $[Pd(NH_3)_4]Cl_2$, into the relatively insoluble dichlorodiammine, $[Pd(NH_3)_2Cl_2]$. Hydrochloric acid is added until no more of the yellow salt forms. A large excess of acid and much heating are to be avoided, as the ammine compound may otherwise be partially decomposed with a resulting unsatisfactory yield of precipitate. The yellow salt settles rapidly and is separated from the mother-liquor by draining on a suitable suction filter,

such as a suction funnel, and washing with cold water. For the next step in the purification, the salt is suspended in water and redissolved by adding ammonium hydroxide and heating. The process of reprecipitation is repeated as often as may be necessary. For the last step, it may be desirable to avoid contamination with the impurities which are apt to be present in ammonium hydroxide by suspending the salt in water and passing in a current of ammonia generated from a flask of ammonium hydroxide.

If palladium of the very highest purity is to be prepared, it is probably desirable to follow the several reprecipitations of palladium dichlorodiammine by one or more precipitations of ammonium chloropalladate. If this is to be done, the yellow salt is dried and ignited to sponge in an atmosphere of hydrogen. The sponge is dissolved in aqua regia and the excess of acid eliminated by evaporation as before. The residue is diluted and filtered to remove silica or other insoluble matter which may have been introduced by the previous operations involving alkaline soln. The vol. of the soln. is adjusted to contain 100 grms. or more of palladium per litre. An equal vol. of sat. soln. of ammonium chloride, and one-third as much nitric acid of sp. gr. 1·42, are added, and the whole soln. is then digested in a covered dish on the steam-bath, until the palladium is precipitated as the crystalline, red ammonium chloropalladate, $(NH_4)_2PdCl_6$. The precipitation can be made so nearly complete as to leave a mother-liquor which is almost colourless. The salt is filtered off on a suction funnel and washed with a 20 per cent. soln. of ammonium chloride. If a second precipitation is to be made, the salt is ignited to sponge and redissolved in aqua regia. This method of purification aids in the removal of base-metal impurities, particularly those which remain dissolved in an ammoniacal soln., but does not tend to eliminate platinum metals rapidly.

The progress of purification can be followed by examining the metals remaining in the mother-liquors from each precipitation. To do this the mother-liquors are evaporated to dryness on the steam-bath and the residues digested with nitric acid to destroy ammonium chloride. After this treatment the soln. is again evaporated to dryness and the residue transferred completely to a crucible and ignited under hydrogen. This is necessary to decompose the ammines of platinum and some of the other metals, which do not respond to the usual qualitative reactions for these metals. After the ignition, the residue is digested with aqua regia and examined for such metals as are thought to be present. Platinum and copper are likely to be the last metals to be eliminated.

Metallic palladium can be obtained by igniting palladous diamminochloride, or ammonium chloropalladite in a current of hydrogen; similarly, the ignition of the cyanide, or iodide yields the metal. E. H. Keiser and M. B. Breed observed that when ammonium chloropalladite or palladous diamminochloride is reduced to metal by heating it in hydrogen, no loss of palladium by volatilization or decrepitation occurs. The metal can be precipitated from soln. of its salts by many reducing agents—formic acid, zinc and hydrochloric acid, etc. The metal can be fused in the oxyhydrogen flame, or in a high temp. furnace. W. H. Wollaston obtained the metal in a compact mass by the method he employed for malleable platinum (*q.v.*). C. W. Davis discussed the recovery of palladium from jewellers' scrap. The satisfactory precipitation of palladium in the presence of rhodium and iridium, by dimethylglyoxime, is described by M. Wunder and V. Thüringer, W. H. Swanger, and R. Gilchrist.

E. H. Keiser and M. B. Breed prepared ammonium chloropalladite from palladium dichloride purified by distillation in a current of chlorine. They also obtained it by dissolving palladium in aqua regia, evaporating the liquid to dryness to remove acid; extracting the mass with water acidulated with hydrochloric acid; and treating the filtered soln. with an excess of ammonia, heated on the water-bath, filtered, and passing hydrogen chloride into the liquor to precipitate palladous diamminochloride. The washed product is dissolved in aq. ammonia, and reprecipitated with hydrogen chloride. By repeating the process a few times, the palladium can be obtained free from all traces of iron, rhodium, and copper. If gold be present, the soln. in hydrochloric acid is treated with sulphur dioxide and allowed to stand to enable the gold to subside. The soln. of the chloride is then treated with ammonia, etc., as just indicated. K. Hessner studied the recovery of palladium.

Palladium can be obtained by **electrodeposition.** According to E. F. Smith,[2] palladium can be deposited from soln. analogous with those employed for the electrodeposition of platinum. A bright deposit is produced by using a current density of 0·05 amp. and 1·2 volts; otherwise the deposit is spongy. An ammoniacal

soln. of palladous diamminodichloride gives good results. The subject was discussed by E. F. Smith and H. F. Keller, F. Wöhler, L. Schucht, A. Joly and E. Leidié, R. Amberg, and J. Langness. V. Kohlschütter and F. Jakober observed that the superposition of an alternating on a direct current in the electrolysis tends to make the crystalline deposit coarse-grained, and to lessen the percentage current-yield. G. Hänsel studied the electro-refining of palladium when alloyed with silver. H. S. Booth and M. Merlub-Sobel studied the deposition of palladium from soln. of its salts in liquid ammonia.

Palladium can be prepared in different physical states—as the compact metal, in crystals, as spongy palladium, as palladium black, and as colloidal platinum. J. Joly [3] prepared **crystalline palladium** by heating to redness palladium ribbon dusted over with finely-divided topaz by means of an electric current. The topaz is supposed to decompose evolving fluorine which attacks the palladium yielding a fluoride which, in turn, dissociates leaving a residue of the crystalline metal. The crystals resemble those of platinum.

W. H. Wollaston found that the ignition of ammonium chloropalladate or chloropalladite furnishes **spongy palladium.** According to E. Wichers and co-workers, the ignition should be conducted in an atm. The use of hydrogen prevents the oxidation of palladium, which would otherwise occur. On the other hand, the metal should not be cooled in hydrogen because the palladium sponge takes up so great an amount of this gas. The current of hydrogen is therefore interrupted after the ignition is complete but before the metal is cooled. In cooling, the sponge will be partly oxidized, but this can be corrected by moistening it with formic acid and drying at 100° to 150°, or by wetting the sponge with alcohol, igniting the latter, and allowing it to burn off spontaneously. A repetition of either treatment may be necessary. Completely reduced palladium sponge has a uniform light grey colour. T. Graham prepared spongy palladium by the ignition of the cyanide ; and A. J. Berry, by reducing the chloride with sodium formate in hot, aq. soln. J. L. Whitten and D. R. Smith prepared **single crystals** of palladium by drawing ordinary polycrystalline wire down to 0·05, slightly annealing the wire, passing the wire at the rate of 9·4 mm. per hour past two mercury contacts, 25 mm. apart, while a current of from 550 to 600 milli-ampères are passed through the lower, water-cooled contact, and left by the upper contact which was not cooled.

According to L. Mond and co-workers, **palladium black** can be obtained by precipitation from soln. of palladium salts by a reducing agent—*e.g.* sodium formate. Palladium black contains 1·65 per cent. of oxygen which cannot be removed by heating it in vacuo at a dull red-heat, but it must be removed by ignition in a current of hydrogen. Palladium black, dried at 100°, contains 0·72 per cent. of water, and assuming that the 138 vols. of oxygen is present as palladous oxide, the composition of palladium black is Pd, 86·59 per cent. ; PdO, 12·69 ; and H_2O, 0·72 per cent. I. I. Tschukoff and co-workers, E. K. Rideal, and A. A. Pollitt studied the catalytic activity of palladium.

F. C. Phillips prepared **palladized asbestos** in which the finely-divided palladium is spread over asbestos to furnish a very efficient palladium catalyst. It is produced by the method used for platinized asbestos, or by soaking asbestos with a soln. of palladous chloride, adding a few drops of alcohol, and igniting. The process is repeated until the asbestos has increased about 6 per cent. in weight in consequence of the deposition of palladium in the fibres of the asbestos. E. V. Alexeevsky and co-workers soaked asbestos cloth for 12 to 15 hrs. in a soln. of palladous chloride in 2*N*-HCl, dried the product at 100°, reduced it in a furnace, during 12 hrs., by means of hydrogen saturated with moist formaldehyde, cooled in hydrogen, and washed it first with hot and then with cold distilled water for 12 hrs. V. N. Morris and L. H. Reyerson studied the action of **palladized silica.**

N. D. Zelinsky prepared a **zinc-palladium couple** by well washing zinc filings with alcohol, then with dil. sulphuric acid until a vigorous evolution of gas begins,

and finally with water. A 1 to 2 per cent. soln. of palladium chloride, acidified with hydrochloric acid, is poured in, and a thin, adhesive layer of palladium is then deposited on the zinc. This couple is then well washed with alcohol, and when necessary dried. G. R. Levi and R. Haardt discussed the structure of the grains. E. Cohen and T. Strengers did not obtain **explosive palladium** by the action of acid on zinc-palladium alloy.

The **spluttering of palladium** at a high temp. in air, oxygen, nitrogen, and hydrogen, and the cathodic spluttering of the metal in air, and hydrogen, was studied by L. Holborn and F. Austin,[4] and M. Faraday—*vide infra*, volatility of palladium. M. Faraday obtained films by reducing a soln. of the chloride with phosphorus, but not with hydrogen. G. Bredig and F. Fortner prepared **colloidal palladium** by sparking palladium electrodes under ice-cold water containing approximately 0·04 grm. of sodium hydroxide per litre. T. Svedberg also obtained the colloid by the oscillatory discharge—**3.** 23, 10. S. Miyamoto used the silent discharge. N. Castoro prepared the **hydrosol** by reducing the chloride with acrolein; J. Sameshima, coal gas; J. Donau, with carbon monoxide; C. Paal and C. Amberger, and J. Piccard and E. Thomas, with hydrogen; A. Lottermoser, with formaldehyde and potassium carbonate; A. Gutbier, A. Gutbier and H. Weithase, with titanous chloride; and M. Bourguel, A. Gutbier and G. Hofmeier, and G. Hofmeier, hydrazine hydrate. As protective colloid, C. Paal and C. Amberger employed sodium protalbiate or lysalbate; A. Gutbier and co-workers, an extract of Irish moss, or gum arabic; A. Skita and W. A. Meyer, gum arabic; H. Plauson, agar-agar; and C. Amberger, lanolin, and oleic acid. E. Biesalsky and co-workers discussed the preparation of the colloid.

The hydrosol is a brown or very dark brown liquid; and, according to R. Zsigmondy, the colour can be detected in soln. containing 0·0005 per cent. of palladium in layers upwards of 1 cm. thick. D. C. Bah studied the coagulation of the colloid. G. Bredig and F. Fortner observed that the catalytic activity with soln. of hydrogen dioxide is so great that 1 gram-atom in 26,000,000 litres of soln. can be detected. C. Paal and C. Amberger observed that the relative activities of the hydrosols of some platinum metals are: Palladium, 22,000; platinum, 11,850; iridium, 3000; and osmium, very small. A. Gutbier and B. Ottenstein studied the **palladium-stannic oxide-purples** produced with colloidal palladium like purple of Cassius is produced with colloidal gold deposited on stannic oxide. E. Biilmann and A. Klit, and M. Bourguel studied the activity of colloidal palladium; A. de Gregorio y Rocasolano, the ageing of the soln.; and C. Paal and W. Hartmann, the effect of mercury, and of the hydroxides of copper, zinc, and iron. T. Svedberg prepared an **organosol** with isobutyl alcohol as dispersion medium.

G. Hofmeier, and A. Gutbier obtained the **hydrogel,** or solid colloidal palladium, by evaporating over sulphuric acid, in vacuo, an aq. soln. containing gum arabic as protective colloid; and C. Paal and C. Amberger, and G. Langer, by the action of hydrogen on a soln. of palladium chloride at 60° in the presence of sodium lysalbate or protalbate, evaporating dialyzed soln. on the water-bath, and afterwards in vacuo over sulphuric acid. The solid hydrogel readily dissolves in water to form a hydrosol. The hydrosol absorbs hydrogen at 60° to 110°, but gives it up again at 130° to 140° in an atm. of carbon dioxide, for the lysalbate is still undecomposed at this temp. J. Donau observed that a borax bead is coloured black by colloidal palladium.

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§ 3. The Physical Properties of Palladium

Palladium is a silvery-white metal and the **colour** is said to be between that of silver and that of platinum. M. Faraday [1] found that thin films of palladium have various shades of Indian ink by transmitted light ; and A. W. Wright, dark brown. H. St. C. Deville and H. Debray, and W. L. Dudley said that the vapour is green. According to W. Haidinger, the metal occurs in octahedral **crystals** belonging to the cubic system. G. Rose said that the crystals are white, and appear of almost microscopic size attached to laminæ of native gold. W. H. Wol-

laston said that a specimen of native palladium from Brazil had a fibrous structure distinguishing it from the grains of platinum with which it was mixed. The alleged dimorphism of palladium emphasized by G. Rose was shown by L. J. Spencer to be not proven—*vide supra*, allopalladium. The crystals were also discussed by A. Breithaupt, E. F. Glocker, J. F. L. Hausmann, C. C. Leonhard, F. Mohs, and G. B. Sowerby. J. L. Whitten and D. P. Smith studied the corrosion figures of single crystal wires; and L. Holborn and co-workers, and F. E. Carter studied the surface structure of palladium which had been heated to a high temp., polished, and etched with acid. M. Ettisch and co-workers, and M. Polanyi and K. Weissenberg said that the crystals in hard-drawn wires are not regularly arranged as in annealed wires. They show a fibrous structure; and the (100) and (111)-faces are arranged normally to the axis of the wire. E. Schmid and G. Wassermann studied the subject. A. W. Hull found that the **X-radiograms** corresponded with a face-centred cubic lattice with side $a=3{\cdot}950$ A., and a distance of 2·795 A. between the nearest atoms. W. Stenzel and J. Weerts gave $a=3{\cdot}8809$ A. T. Barth and G. Lunde, $a=3{\cdot}873$ A.; E. A. Owen and E. L. Yates, and E. A. Owen and J. Iball gave $a=3{\cdot}8850$ A., and calculated that the closest approach of the atoms is 2·747 A. The subject was discussed by W. L. Bragg, G. Kettmann, and V. I. Iveronova. E. A. Owen and E. L. Yates, F. Krüger and G. Gehm, G. Natta, and J. D. Hanawalt studied the distortion of the lattice by hydrogen, and A. Osawa, the 3·6 to 3·87 per cent. increase in the lattice constant by the adsorption of hydrogen—*vide infra*. T. M. Lowry and R. G. Parker gave 12·0173 for the sp. gr. of massive palladium, and 11·9863 for filings. F. M. Jäger and J. E. Zanstra showed that there are changes in the X-radiogram of palladium corresponding with a transformation from one **allotropic form** to another at 1200°; and thus is in harmony with the sp. ht. data of F. M. Jäger and E. Rosenhohm, and F. M. Jäger. W. P. Davey gave $a=3{\cdot}859$ A.; T. Barth and G. Lunde, $a=3{\cdot}873$ A.; G. Bredig and R. Allolio, $a=3{\cdot}991$ A.; L. W. McKeehan, $a=3{\cdot}900$ A.; S. Holgersson and E. Sedström, $a=3{\cdot}897$ A.; and J. O. Linde and G. Borelius gave $a=3{\cdot}88+0{\cdot}0_446(\theta-20)$ in A. units at $\theta°$. The subject was discussed by R. W. G. Wycoff, K. Weissenberg, and A. E. van Arkel. A. Osawa found that platinum black has the same lattice structure as the compact metal, and that when hydrogenized there is an expansion of the lattice corresponding with the formation of a solid soln. M. Yamada made a similar observation, whilst L. W. McKeehan said that the hydrogenized palladium has two, face-centred, cubic lattices—one of palladium alone with $a=3{\cdot}900$ A., and the other, probably Pd_2H, with $a=4{\cdot}000$ to 4·039 A. L. W. McKeehan, and G. Rosenhall studied the effect of hydrogen on the lattice constant. For J. O. Linde and G. Borelius' observations, *vide infra*, palladium and hydrogen. G. Tammann studied the effect of cold-working.

W. H. Wollaston gave 11·3 to 11·8 for the **specific gravity**; L. N. Vauquelin, 11·8; J. Cloud, 11·041 at 18°; A. Breithaupt, 11·752; W. A. Lampadius, 11·852; E. H. Keiser and M. B. Breed, 11·0; J. Violle, 11·97 at 0°; G. Wolf, 11·78; H. St. C. Deville and H. Debray, 11·4 at 22·5°; L. Troost and P. Hautefeuille, 12·0; K. Lisenko, 12·104; W. J. Cock, 11·30, and for the hammered metal, 11·80; and R. Böttger gave a collection of values. F. Mylius and R. Dietz gave 11·9 for the purified, cast and hammered metal; and W. Jäger and H. Diesselhorst, 11·96 for the purified, cast metal at 18°. G. Quincke gave 10·8 for the sp. gr. of the molten metal. A. W. Hull calculated 11·4 for the sp. gr. of palladium from its lattice constants, when the accepted values range from 11·4 to 11·8; L. W. McKeehan calculated 11·87; and S. Holgersson and E. Sedström, 11·97. V. M. Goldschmidt gave 1·370 A. for the **atomic radius.** W. Hulme-Rothery, E. H. Westling, J. C. Slater, G. Hägg, and W. Biltz and K. Meisel studied the packing density, or atomic radius; and F. G. Mann and D. Purdie, the **parachlor** of palladium. For the effect of hydrogen, *vide infra*, hydrogenized palladium. The **hardness** of native palladium on Mohs' scale is said to be between 4 and 5; J. R. Rydberg gave 4·8. C. A. Edwards gave 61·0 for Brinell's hardness;

F. E. Carter gave 52 for the cast metal, 109 for the hard, and 49 for the annealed metal; and for the scleroscopic hardness, 25 for the hard, and 8 for the annealed metal. T. Turner, and C. Johnson discussed the subject. G. Tammann and co-workers studied the effect of cold-work. S. Cowper-Coles said that electro-deposited palladium is as hard as nickel.

According to W. H. Wollaston,[2] the palladium he prepared was rather less ductile than platinum, and it can be rolled out into thin leaves. G. Wertheim gave 9709 kgrms. per sq. mm. for the **elastic modulus** of palladium; C. Schäffer, 11·284 kgrms. per sq. mm.; A. Wassmuth gave $E=1{\cdot}123\times10^{12}$ c.g.s. units for purified palladium; and E. Grüneisen obtained 11,760, 11,550, 11,470, and 11,480 kgrms. per sq. mm., at 15·1° to 19°, by different methods. F. E. Carter gave 12,000 kgrms. per sq. mm. for hard, and 9750 kgrms. per sq. mm. for annealed palladium. The temp. coeff. of the elastic modulus observed by C. Schäffer is 1·979 per cent. for temp. between 20° and −186°; and A. Wassmuth gave $dE/E.dT=2{\cdot}05\times10^{-4}$. A. Mallock said that the ratio of Young's modulus of elasticity at −273° and 0° is 1·27. P. Lasareff found the elastic limit to be proportional to $n^{5/3}$, where n is the number of atoms per c.c. For the effect of hydrogen, *vide infra*, hydrogenized palladium. K. R. Koch measured the ratio of the electrical resistance of five samples of palladium before and after saturation with hydrogen, R_0/R; he also measured the percentage changes in length δl and sectional area, δa, and in the moduli of tension, E, and torsion, n:

R_0/R	δl	δa	E	n
1·65	5·0	7·0	−10·5	−16·5
2·10	8·0	3·0	−12·5	−13·0
1·98	5·0	5·0	−10·0	−12·0
1·59	1·7	1·8	−21·0	−10·0
1·84	2·3	1·2	−12·0	−14·0

C. Schäffer found the torsion modulus of purified palladium to be $F=4613{\cdot}7$ kgrms. per sq. mm. at room temp., and Poisson's ratio is 0·223. The value of the torsion modulus decreases 2·696 per cent. per 100° fall of temp. A. Wassmuth gave for purified palladium, $F=5103$ kgrms. per sq. mm., and $dF/F.dT=2{\cdot}9\times10^{-4}$. C. E. Guye and H. Schapper studied the effect of temp. on the torsion modulus; and P. W. Bridgman observed that the rigidity increases 1·08 per cent. for a press. of 10,000 kgrms. per sq. cm. E. Grüneisen observed $F=5210$ kgrms. per sq. mm.; E. Widder gave $E=E_{20}\{1-0{\cdot}0006536(\theta-20)\}$; and K. R. Koch and C. Dannecker, Fig. 1,

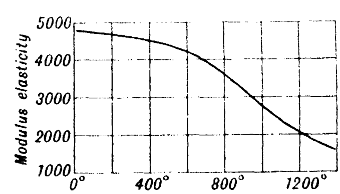

Fig. 1.—The Effect of Temperature on the Elastic Modulus of Palladium.

	20°	200°	400°	600°	800°	1000°	1200°	1400°
F . .	4900	4870	4690	4260	3700	2790	2080	1520

T. Graham observed that the **tensile strength** of a palladium wire 100 mm. long, and weighing 0·1987 grm. is 10 kgrms.; and W. Giebel observed that a wire of the purified metal, 1 mm. diameter, broke with a load of 30 kgrms. J. L. Whitten and D. P. Smith found that the elongation with single crystals of palladium varied from 0·7 to 4·0 per cent. as compared with less than 0·2 per cent. for polycrystalline wire. F. E. Carter gave 39 kgrms. per sq. mm. for hard, and 14 kgrms. per sq. mm. for 0·5 mm. wire of annealed palladium, with a 1 per cent. elongation in 2 inches for soft, and 24 per cent. for annealed palladium; the **volume elasticity** of cast palladium is 17·6 dynes per sq. cm.; Ericsen's **ductility** test of hard palladium is 7·6 mm., and of the annealed metal, 12·0. G. Tammann discussed the effect of cold-work on the physical properties; and E. M. Wise and J. T. Eash studied the mechanical properties of palladium—cold-drawn, and annealed at 800°. The **rigidity** is 5·11 dynes per sq. cm.; and **Poissan's ratio** is 0·393. J. L. Whitten

and D. P. Smith found that on breaking single crystal wires in tension, the elongation varied from 0·7 to 4·0 per cent. as compared with $<0{\cdot}2$ per cent. for an ordinary polycrystalline wire. For the effect of hydrogen, *vide infra*, hydrogenized palladium. Owing to changes in the mechanical strengths of palladium in the vicinity of 8° below the m.p., G. Ribaud and S. Nikitine assumed that an **allotropic transformation** occurs—*vide infra*, sp. ht.

T. W. Richards gave 18,800 megabars for the **internal pressure** of palladium at 20°. R. von D. Wegner, and G. A. Tomlinson studied the internal cohesion. T. W. Richards found the **compressibility** to be $0{\cdot}38\times10^{-6}$ per 0·987 atm. E. Grüneisen obtained a similar result; L. H. Adams gave $0{\cdot}53\times10^{-6}$ megabar; and P. W. Bridgman gave $5{\cdot}19\times10^{-7}$ to $5{\cdot}28\times10^{-7}$ for the compressibility of palladium; and for the effect of press. and temp., he observed that for a specimen of massive palladium, $dv/v=-0{\cdot}0_7519p+0{\cdot}0_{12}210p^2$ at 30° $dv/v=-0{\cdot}0_7511p+0{\cdot}0_{12}20p^2$ at 75°; and with drawn wire, $dv/v=-0{\cdot}0_7528p-0{\cdot}0_{12}210p^2$ at 30°, and $dv/v=0{\cdot}0_7531p+0{\cdot}0_{12}210p^2$ at 75°. R. H. Mehl studied the cohesion press. The **velocity of sound** in palladium is 3150 metres per second at 20°.

H. Fizeau [3] found the coeff. of **thermal expansion** to be $0{\cdot}0_41180$ at 20°, and $0{\cdot}0_41176$ at 40°; and K. Scheel found the length l of a palladium rod at θ° between −190° and 100° to be $l=l_0(1+0{\cdot}0_411521\theta+0{\cdot}0_851676\theta^2-0{\cdot}0_{10}1124\theta^3)$; and L. Holborn and A. L. Day gave $l=l_0(1+0{\cdot}0_411676\theta+0{\cdot}0_821876\theta^2)$, between 0° and 1000°. H. Holzmann gave $0{\cdot}0_410637+0{\cdot}0_89187(\theta-20°)$, and E. Grüneisen, $\alpha=0{\cdot}0_41027$ at −190° to 17°, and $0{\cdot}0_41188$ at 17° to 100°. G. Wiedemann and R. Franz observed that if the **thermal conductivity** of silver is 100, that of palladium is 7·3 in vacuo, and 6·3 in air. W. Jäger and H. Diesselhorst gave for the thermal conductivity of palladium, k cals. per cm. per second per degree, $k=0{\cdot}1682$ at 18°, and $k=0{\cdot}1776$ at 100°; whilst T. Barratt and R. M. Winter gave for the purified metal $k=0{\cdot}44$ at 17° and 0·143 at 100°; and for the commercial metal $k=1{\cdot}101$ at 17° and 0·100 at 100°. H. Grüneisen and H. Reddemann studied the low temp. conductivity. P. W. Bridgman found that for a tensile load of 770 kgrms. per sq. cm., the proportional change in thermal conductivity is $-0{\cdot}20\times10^{-6}$.

H. V. Regnault [4] found that the **specific heat** of palladium is 0·05928 between 0° and 100°. J. Violle obtained for the mean sp. ht. at θ° between 0° and 1265°, $c=0{\cdot}0582+0{\cdot}0_410\theta$, and for the true sp. ht. at θ°, $c_p=0{\cdot}0582+0{\cdot}0_420\theta$. H. Holzmann gave $c=0{\cdot}0584+0{\cdot}000015853$. V. Behn gave 0·0567 between −79° and 18°, and 0·0528 between −186° and 18°; J. Dewar gave 0·0190 between −253° and −196°; T. W. Richards and F. G. Jackson, 0·0517 between −188° and 20°; and W. Jäger and H. Diesselhorst, 0·0586 at 18°, and 0·0617 at 100°. E. Grüneisen gave $c_p=0{\cdot}0520$ at −190° to 17°, and 0·0601 from 17° to 100°; E. H. Hall made observations on the subject. F. M. Jäger and co-workers found the true sp. hts. and the at. hts. between 0° and 1550° to be:

	0°	100°	300°	500°	700°
c_p	0·05377	0·05640	0·06118	0·06534	0·06885
c_v	0·05250	0·05250	0·05857	0·06180	0·06437
C_p	5·737	6·018	6·528	6·971	7·346
C_v	5·602	5·836	6·249	6·594	6·868

	900°	1100°	1300°	1550°
c_p	0·07173	0·07398	0·07559	(0·07639)
c_v	0·06628	0·06749	0·06799	(0·06727)
C_p	7·654	7·894	8·066	(8·151)
C_v	7·072	7·196	7·251	(7·071)

There is a maximum in the curve for $c_p=0{\cdot}07664$ at 1520°, but F. M. Jäger said that the evidence does not prove the existence of an allotropic form; nor did A. L. Day and R. B. Sosman detect any evidence of allotropic change in their measurements of the thermoelectric force—*vide supra*, tensile strength. The true sp. hts. were represented by F. M. Jäger and W. A. Veenstra by $c_p=0{\cdot}058378+0{\cdot}0_4602746\theta-0{\cdot}0_98602\theta^2$, which has a maximum at 1520° and $c_p=0{\cdot}07664$.

The **atomic heat** at 100° approximates $3R$, but at 1520° it has the values $C_p=8{\cdot}177$ and $C_v=7{\cdot}225$; and F. M. Jäger and W. A. Veenstra gave $C_p=6{\cdot}2288+0{\cdot}012862\theta+0{\cdot}0_6275280\theta^2$. J. Maydel discussed the general formula.

R. C. Smith [5] observed that the sintering of precipitated palladium-black occurs at about 600°. E. Biewend, and J. R. Bréant observed that palladium shows signs of fusion at about the temp. of molten iron; L. N. Vauquelin melted the metal on a piece of charcoal ignited in a stream of oxygen; and E. Becquerel said that palladium melts at a lower temp. than any other platinum metal. J. L. Byers studied the behaviour of the metal on cupellation. J. Violle estimated the **melting point** of palladium to be 1500°; and E. Becquerel, 1460° to 1480°. L. Holborn and S. Valentiner gave 1572·9° for the m.p.; W. Nernst and H. von Wartenberg gave 1552°; C. W. Waidner and G. K. Burgess, and F. E. Carter, 1550°; E. Brodhun and F. Hoffmann, 1557°; F. M. Jäger and E. Rosenbohm, 1549·2°; L. Holborn and F. Henning, 1535° to 1549°; L. Holborn and W. Wien, 1587°; G. Holst and E. Oosterhuis, 1577°; F. Hoffmann and W. Meissner, 1557°; F. H. Schofield, and L. D. Morris and S. R. Scholes, 1555°; E. P. Hyde and W. E. Forsythe obtained a very high value; E. P. Hyde and co-workers, 1557°; F. Weibke and J. Laar, 1553°; A. L. Day and R. B. Sosman, 1550°; C. E. Mendenhall, 1553°; and C. E. Mendenhall and L. R. Ingersoll, 1548° (m.p. of platinum 1745°) or 1576° (m.p. of platinum 1789°); F. S. Tritton and D. Hanson, 1555°; G. K. Burgess and R. G. Waltenberg, 1549°; C. H. M. Jenkins and M. L. V. Gayler, 1539°; W. R. Mott, estimated 1549°; L. I. Dana and P. D. Foote, 1550°; W. Guertler and M. Pirani, 1545°; and F. H. Schofield gave 1555° with gold 1063°. Observations were made by K. Scheel. C. O. Fairchild and co-workers calculated 1553°±0·7° as the best representative value from recent determinations, and they obtained 1553·6° when the m.p. of gold is 1063°. C. E. Mendenhall and C. L. Utterback found that the presence of traces of platinum is the cause of some discrepant observations. R. Wright and R. C. Smith studied the sintering of the finely-divided metal. C. E. Mendenhall and L. R. Ingersoll observed that palladium may be undercooled; and that when the molten metal solidifies, there is a momentary flash of light. G. Ribaud and S. Nikitine found that the m.p. is lowered 8° by a mechanical tension greater than 2·5 grms. per sq. mm. A. Stein discussed the relationship between the at. vol., m.p., and electrical resistance; P. W. Robertson, between the m.p. and the at. vol.; T. Carnelley, the relation between the m.p. and thermal expansion; W. Herz, the relation between the m.p. and the vibration frequency; and J. Johnston, the effect of press. on the m.p. If Q be the heat of fusion per gram, T the absolute m.p., and D the density at the m.p., then from thermodynamics, the pressure p on atm. required to melt palladium at 27° is 31,000.

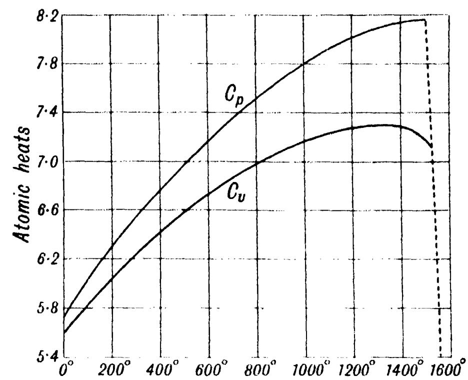

FIG. 2.—Atomic Heat Curves of Palladium.

W. Crookes found that palladium loses 0·6 per cent. in weight when heated in air at 1300° for 30 hrs. The volatility at 1300°, in air, is three times that of platinum. The subject was studied by L. Holborn and co-workers—*vide* platinum. The results were:

Time		2	6	10	14	18	22	26	30 hrs.
Loss	1300°	0·117	0·314	0·424	0·495	0·574	0·629	0·692	0·745 per cent.
	900°	0·0159	0·0513	0·0919	0·1184	0·1396	0·1626	0·1785	0·1827 „

F. E. Carter said that appreciable volatilization occurs at 1000°; and A. Knocke observed in vacuo an appreciable volatilization at 735°. W. Stewart, and L. Holborn and L. Austin showed that, unlike the case of platinum, the rate of loss in weight of palladium in oxygen increases with a decrease of press., and is practically independent of the nature of the surrounding gas. The deposit is always black when oxygen is present, but is bright and metallic in hydrogen at 1·25 mm. press. J. H. T. Roberts showed that the phenomenon with palladium is not due to the escape of occluded gas, and the bright deposits in hydrogen are not due to the reduction of an oxide; rather is the effect due to a simple volatilization of the palladium. H. Moissan found that in the electric arc furnace palladium vaporizes and the vapour condenses in small crystals and in globules. W. R. Mott estimated the **boiling point** of palladium to be 3000°, but 2200° is considered to be nearer the mark. F. E. Carter gave 2540° for the b.p.

C. M. Guldberg calculated the **critical temperature** of palladium to be 5700°. J. Violle, and J. W. Richards estimated the **heat of fusion** of palladium to be 36·3 cals.; or 10·8 kilograles per gram-atom; and F. M. Jäger and E. Rosenbohm gave 20 cals. per gram. N. von Raschevsky, and N. F. Deerr made observations on this subject. A. D. van Riemsdijk studied the flashing which occurs on cupellation. G. N. Lewis and co-workers gave 8·80 to 8·90 cals. for the **entropy** of palladium at 25°; and E. D. Eastman calculated 8·5 to 9·1 cals. at 25°. The entropy and internal energy were studied by R. D. Kleeman, R. von D. Wegener, K. K. Kelley, W. Herz, and E. Kordes; and the thermal energy by R. Nübel.

H. von Wartenberg found the **index of refraction,** μ, of purified palladium to be 1·62 for light of wave-length $\lambda=579\mu\mu$; the index of absorption $k=2{\cdot}11$; the absorption coeff., $\mu k=3{\cdot}41$; and the **reflecting power,** $R=65$ per cent. B. Pogany gave for a cathodic spluttered film, $232\mu\mu$ thick:

λ . . .	700	650	600	550	$500\mu\mu$
μ . . .	2·05	1·94	1·84	1·76	1·74
μk . . .	2·86	2·74	2·60	2·40	2·16

For a layer $600\mu\mu$ thick, K. Försterling obtained the results summarized in Fig. 3. R. Hamer, and A. de Gramont studied the reflecting power of thin films, etc. E. O. Hulbert found the reflecting power for ultra-violet rays to be:

λ . . .	188	200	251	305	357
R . . .	16	18	20	22	26 per cent.

The **emissivity** is 0·38 for $\lambda=0{\cdot}55\mu$ and 0·33 for $\lambda=0{\cdot}65\mu$ with the solid, and 0·37 for $\lambda=0{\cdot}65\mu$ for the liquid. F. Henning, F. Henning and W. Heuse, E. Wiegand, G. Holst and E. Oosterhuis, E. Brodhun and F. Hoffmann, G. Ribaud and S. Nikitine, and S. Nikitine studied the black body **radiation** of palladium at the m.p.; and W. Zobel observed a maximum temp. of radiation with palladium which has been heated in air. This temp. is the temp. at which the oxide film is broken up and the palladium recrystallized. F. Hoffmann and W. Meissner studied the relative brightness of the dark radiation of gold and palladium at their m.p. B. Pogany studied the **Faraday effect** with spluttered films.

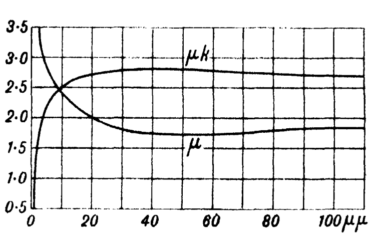

FIG. 3.—Indices of Refraction of Palladium.

The difficulties attending the purification of palladium render some of the early observations on the spectrum of little value—*e.g.* those of T. R. Robinson.[6] A. Mitscherlich did not succeed in obtaining a **flame spectrum.** W. N. Hartley and H. Ramage observed some bands in the oxy-hydrogen flame. Observations on the **spark spectrum** were made by W. A. Miller, G. Kirchhoff, W. Huggins, R. Thalen,

L. de Boisbaudran, J. Parry and A. E. Tucker, W. N. Hartley, E. Demarçay, H. Nagaoka and co-workers, H. A. Blair, K. Bechert and M. A. Catalan, A. G. Shenstone, P. E. Dhein, W. Kraemer, G. Kail, W. E. Adeney, O. Lohse, A. Hagenbach and H. Konen, H. W. Morse, J. M. Eder and E. Valenta, and C. E. Gissing. F. Exner and E. Haschek found the more intense lines in the spark spectrum to be 2776·95, 2854·70, 3404·80, 3421·41, 3481·34, 3517·11, 3553·21, 3609·70, 3634·83, 3894·39, and 4213·16. The spark spectrum with a soln. of palladium chloride was found by J. Formanek to have the characteristic lines, Fig. 4, 5736, and a double line 5695

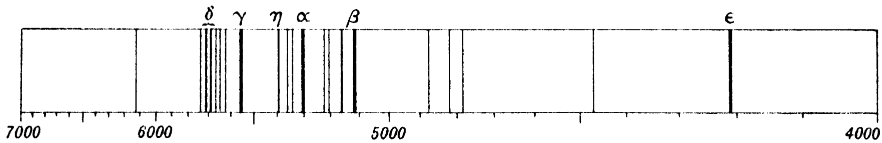

FIG. 4.—The Spark Spectrum of Palladium.

and 5669(δ) in the yellowish-green; 5547(γ), 5395(η), 5296(α), 5164, and 5117(β) in the green; 4875, 4818, 4788, and 4474 in the blue; and 4213(ε) in the violet. The lines α, β, and γ are characteristic. L. H. G. Clark and E. Cohen, and W. F. Meggers and O. Laporte studied the under-water, spark spectrum. F. Exner and E. Haschek gave for the more intense lines in the **arc spectrum** of palladium: 3028·05, 3065·41, 3119·19, 3302·28, 3373·21, 3404·73, 3421·42, 3460·93, 3481·31, 3517·08, 3553·24, 3609·71, 3634·85, 3690·49, 3894·33, 3958·79, 4213·11, 5163·99, 5295·83, 5395·47, 5543·04, 5670·28, and 6784·80. Observations were also made by C. S. Beals, A. G. Shenstone, H. A. Rowland and R. R. Tatnall, H. Kayser, W. F. Meggers, J. M. Eder and E. Valenta, K. Bechert and M. A. Catalan, and A. Hagenbach and H. Konen.

H. A. Rowland, and J. N. Lockyer studied the **solar spectrum.** The **ultra-violet spectrum** was examined by F. Exner and E. Haschek, G. Kail, W. A. Miller, and V. Schumann. J. N. Lockyer and W. C. Roberts-Austen, and J. C. McLennan and co-workers examined the **absorption spectrum** of the vapour of palladium; and R. Samuel, the absorption spectra of soln. of complex salts. The spectrum of the **cathode light** emitted by palladium electrodes by strong currents was investigated by W. von Bolton. W. J. Humphreys studied the effect of *pressure* on the emission spectrum of palladium; and J. E. Purvis, M. A. Levitskaya, C. S. Beals, and C. Peterke, the effect of a *magnetic field*—the **Zeeman effect.** W. Gerlach and co-workers discussed the most sensitive lines for the recognition of palladium. J. C. McLennan and H. G. Smith, C. S. Beals, M. A. Levitskaya, C. P. Snyder, J. E. Mack, O. Laporte, G. K. Schoepfle, C. C. Kiess and O. Laporte, O. Laporte and D. R. Inglis, M. Kimura and G. Nakamura, P. G. Kruger and W. E. Shoupp, E. Paulson, L. Sibaiya, and P. G. Nutting studied the **series spectra** or the structure of the spectrum, or regularities in the orientation of the lines.

J. Formanek observed that conc. aq. soln. of palladous chloride or nitrate are brownish-yellow, and absorb almost all the visible spectrum up to the red; no bands appear when the soln. is diluted. If a few drops of tincture of alkanna be added to a not too dil. soln. of palladous chloride, the original red liquid becomes orange-yellow, then steel-grey, and in 15 or 20 minutes, green. The absorption spectrum of the soln. changes in a corresponding manner. The absorption spectrum is displaced towards the red, and remains stationary when the liquid is green. The absorption spectrum then has the principal band at 6418, and two secondary bands at 5875 and 5447. After the soln. has been allowed to stand for some time, it becomes turbid, and no longer exhibits the absorption spectrum of palladium. If a trace of ammonia be added to the green liquid, the absorption spectrum does not change, but if a few drops of ammonia be added in excess, the liquid becomes blue, and another absorption spectrum appears with the chief band at 6084, and secondary bands at 5629 and 5234. This absorption spectrum soon decreases in

intensity and gradually disappears leaving a red liquid which shows the absorption spectrum of alkanna. R. Samuel and A. R. R. Despande studied the absorption spectra of soln. of palladium salts.

The K- series of the **X-ray spectrum** was found by M. Siegbahn,[7] G. B. Deodhar, W. Bothe and H. Fränz, P. A. Ross, J. H. Williams, S. K. Allison, B. A. Wooten, G. Réchou, P. Nasledoff and P. Scharawsky, D. Coster, A. Leide, K. Lang, G. Kellström, E. Nähring, W. W. Hansen and K. B. Stoddard, and A. Sommerfeld to exhibit lines corresponding with $\alpha_1\alpha$=0·584266; $\alpha_2\alpha^1$=0·588632; $\beta_1\beta$=0·519474; $\beta_2\gamma$=0·509181; β_3=0·520093; A. Leide gave β_3=0·52010, and β_4=0·50790. M. Siegbahn, E. Friman, and A. Sommerfeld gave for the L-series, $\alpha_1\alpha$=4·35850; $\alpha_2\alpha'$=4·36660; $\alpha_3\alpha''$=4·344; $l\epsilon$=4·9396; $\eta_1\eta$=4·6502; L_I=3·4206; L_{II}=3·7152; L_{III}=3·9005; $\beta_1\beta$=4·13730; $\beta_2\gamma$=3·9007; $\beta_3\phi$=4·0257; $\beta_4\phi'$=4·0623; $\beta_6\iota$ =4·0070; β_{11}=3·8676; and β_{12}=3·8567; $\gamma_1\delta$=3·71636; $\eta_2\chi$ and $\gamma_3\chi$=3·4809; $\gamma_5\kappa$=3·8116; and γ_7=3·676. F. K. and R. D. Richtmyer gave α_1=4·3565; α^I=4·3453; α^{II}=4·3412; α^{III}=4·3359; α^{IV}=4·3291; α^V=4·3222; and α^{VI}=4·3142; and M. J. Druyvesteyn, β_2=3·9007; β'_2=3·8688; β''_2=3·8574; γ_1=3·7164; and γ'_2=3·678 A. G. D. van Dyke and G. A. Lindsay, B. B. Ray, A. Jönsson, F. R. Hirsh and F. K. Richtmyer, D. Coster, K. Lang, W. Bothe and H. Fränz, F. C. and L. P. Chalklin, J. Zahradnicek, and J. D. Hanawalt studied the L-series; and C. G. Barkla, the J-phenomena. G. Harker [8] found that X-rays, and γ-radiations stimulate the catalytic activity of palladium in hydrogenations. E. Nähring examined the effect of hydrogen on the X-ray lines of hydrogenized palladium. N. I. Koboseff and V. L. Anochin studied the desorption of hydrogen and oxygen in palladium by electronic bombardment; R. Kollath, the production of protons from hydrogen occluded a palladium when bombarded by electrons; and M. Wolfke and J. Rolinsky, the emission of positive ions at about 1200°—probably alkali metals—which ceases after a few hours' heating. T. Kinbara observed the effect of a current with a palladium pole on a photographic dry plate.

E. C. Stoner and L. H. Martin [9] studied the absorption of X-rays by palladium. F. C. and L. P. Chalklin, L. P. Davies, V. Nakaya, O. W. Richardson and F. S. Robertson, and L. P. Davies studied the emission of soft X-rays by palladium; E. Nähring, the scattering; Y. F. Cheng, the polarization; D. A. McInnes and T. Shedlovsky, and D. Nasledoff and P. Scharawsky, the intensity of the lines; D. Coster, the energy levels of the X-ray spectra; R. A. Rogers, the resistance of thin films exposed to X-rays; O. Laporte, the screening constants; H. E. Farnsworth, the effect of electronic bombardment; and L. Tonks, the anchoring of the cathode spot in the discharge tube by palladium projecting through a mercury surface. The emission of electrons was investigated by W. Espe,[10] W. W. Hansen and K. B. Stoddard, and J. F. Chittum; the emission of positive ions by F. Gulbis; the limiting frequency by S. Björek, and J. E. P. Wagstaff; the scattering of γ-rays, by T. Heiting; the excitation of secondary radiation by slow cathode rays, by H. W. Langenwalther; artificial radioactivity, by E. Fermi and co-workers, and E. Amaldi and co-workers; and the Moser rays, by N. Piltschikoff.

G. L. Locker,[11] H. Hulubei, L. A. du Bridge and W. W. Rocher, R. S. Bartlett, W. Bennewitz, P. A. Maidstone, and T. Pavolini studied the photoelectric effect. T. Pavolini studied the photosensitivity. K. Reger, W. Bennewitz, J Kluge, R. S. Bartlett, G. Bethe, and H. Klumb studied the effect of adsorbed gas on the photoelectric effect of palladium. W. Frese noted that any treatment which renders the metal passive reduces the photoelectric sensitiveness. According to L. A. du Bridge and W. W. Roehr, the photoelectric threshold of platinum during 100 hrs.' heat treatment in vacuo shifted from an initial value below 2300 A. to a maximum over 3022 A., and finally assumed a steady state at 2486 A. with 4·97 volts. The thermionic work function is 4·99 volts. L. A. du Bridge and W. W. Roehr studied the subject. F. H. Newman and H. J. Walke, J. C. McLennan and co-workers, and K. A. Hofmann and co-workers studied the induced radioactivity of palladium.

P. A. Maidstone[12] studied the effect of heat treatment on the frictional electric charge. If the **electrical conductivity** of silver be 100, E. Becquerel said that the conductivity of palladium is 13·97, and A. Matthiessen, 12·64 at 17·2°. J. Dewar and J. A. Flemming gave $9 \cdot 8 \times 10^4$ mhos per cm. cube for the electrical conductivity of palladium at 10°; C. G. Knott gave $9 \cdot 4 \times 10^4$ mhos at 0°; and W. Jäger and H. Diesselhorst, $9 \cdot 33 \times 10^4$ mhos at 18°, and $7 \cdot 27 \times 10^4$ mhos at 100°. J. Dewar and J. A. Flemming gave for the temp. coeff. of the electrical resistance between 0° and 100°, 0·00354; W. Jäger and H. Diesselhorst, 0·00368; L. Holborn, 0·00377; and P. W. Bridgman, 0·003178—a low value due to the presence of impurities. Observations were made by E. Grüneisen, and A. Schulze. F. E. Carter gave 0·0037 for hard palladium between 0° and 100°; 0·00236 for annealed palladium between 0° and 1200°. There is a 0·001 per cent. increase in a magnetic field of 10,000 gauss. W. Meissner and B. Voigt studied the superconductivity of palladium at low temp. H. Rolnick measured the effect of tension on the resistance. H. Jellinek, A. Puodziukynas, and M. E. Klarmann observed that the effect of absorbed argon and neon is to increase the resistance, *vide infra*, for the effect of hydrogen, also *vide supra*, tensile strength. D. P. Smith said that oxygen lowers the electrical resistance. A. Stein discussed the relationship between the at. vol., m.p., and electrical resistance. R. S. Bartlett observed that the decrease in the resistance of thin films of palladium in light from a quartz mercury lamp is 14×10^{-6}. B. Pogany found that the resistance of films obtained by cathodic sputtering increases with a decrease in the thickness of the film. G. Tammann and K. L. Dreyer studied the effect of cold-work. P. W. Bridgman found that the effect of press., p kgrms. per sq. cm., is:

		0°	25°	50°	75°	100°
Resistance		1·000	1·0810	1·1609	1·2388	1·3178
Press. coeff.	at 0 kgrm.	$-0 \cdot 0_5 1983$	$-0 \cdot 0_5 1965$	$-0 \cdot 0_5 1945$	$-0 \cdot 0_5 1920$	$-0 \cdot 0_5 1895$
	at 12,000 kgrms.	$-0 \cdot 0_5 1855$	$-0 \cdot 0_5 1840$	$-0 \cdot 0_5 1830$	$-0 \cdot 0_5 1825$	$-0 \cdot 0_5 1830$
	Average	$-0 \cdot 0_5 1895$	$-0 \cdot 0_5 1887$	$-0 \cdot 0_5 1879$	$-0 \cdot 0_5 1871$	$-0 \cdot 0_5 1863$

Like platinum, but unlike most other metals, there is an abnormal deviation of the resistance from linearity with temp.; the slope of the resistance-temp. curve is greater at 0° than it is at 100°. The press. coeff. at 0°, —78·4°, and —182·9°, and 7000 kgrms. per sq. mm. were respectively $-0 \cdot 0_5 213$, $-0 \cdot 0_5 232$, and $-0 \cdot 0_5 282$. Measurements were also made by A. Coehn and H. Jürgens, W. Meissner and B. Voigt, N. F. Mott, J. O. Linde, and K. Honda and co-workers. J. T. MacGregor-Morris and R. P. Hunt studied the temp. coeff. of the resistance. B. Beckman gave $0 \cdot 0_5 219$ for the press. coeff. at 0°; and P. W. Bridgman, $0 \cdot 0_5 1983$. P. W. Bridgman gave $1 \cdot 37 \times 10^{-6}$ for the corrected longitudinal fractional change of resistance per kilogram per sq. cm., and $0 \cdot 5 \times 10^{-6}$ for the transverse fractional change of resistance. For a tensile load of 770 kgrms. per sq. cm. the proportional change in sp. electrical conductivity is $-1 \cdot 52 \times 10^{-6}$, and for a load of 457 kgrms. per sq. cm., $-1 \cdot 66 \times 10^{-6}$. H. Rolnick measured the effect of tension; and P. Kapitza, the effect of a magnetic field. G. Tammann and co-workers studied the effect of cold work; H. Reddemann, the relation with the thermal conductivity; R. A. Rogers, the effect of X-rays; E. A. Harding and D. P. Smith, D. P. Smith, A. Coehn, and H. Hagen and A. Seiverts, the effect of the occlusion of oxygen on the resistance of palladium; and C. A. Knorr and E. Schwartz, D. P. Smith and others for the effect of hydrogen, *vide infra*, hydrogenized palladium. O. E. Branby observed the unipolar conductivity of the condenser Ag–Mica–Pd. A. T. Waterman, F. Simon, and A. Coehn and W. Specht studied the theory of electrical conductivity. According to J. Shields,[13] the e.m.f. of the combination—palladium containing a small quantity of hydrogen | dilute sulphuric acid | palladium containing a large quantity of hydrogen—is zero, or nearly so. Thus, the cell does not behave like a true concentration cell, as would probably be the case were the absorption of hydrogen by palladium simply a process of soln. The view

that a chemical compound is formed agrees better with the facts, for the e.m.f. in this case would be independent of the quantity of compound formed. J. A. Kendall studied the e.m.f. of the cell with hydrogenized palladium and palladium. S. J. French and L. Kahlenberg observed the effect of gases on the electrode potential of palladium in N-KCl. With hydrogen or nitrogen, the potential becomes more basic reaching a maximum, and then falling off; and with oxygen, there is very little change. Carbon monoxide, and methane also alter the potential of palladium, and helium has a slight effect. L. Kahlenberg and J. V. Steinle observed the single potential of palladium in $0{\cdot}5N$-Na_3AsO_4 to be 0·861 volt; in $0{\cdot}5N$-K_3AsO_4, 0·1870 volt; and in N-KCl, sat. with arsenic trioxide, 0·872 volt. F. Braun studied the electrolyses of soln. of palladium salts. R. Köhler studied the hydrogen potential; A. Voet, the anodic dispersion; J. C. Andrews, the hydrogen electrode; and J. Sambussy, the potential in nitrobenzene. E. Biilmann and A. Klit found that a little colloidal palladium hinders the polarization of H$^{\cdot}$-electrodes of platinum.

C. G. Müller [14] observed that in the electrolytic gas cell with palladium in place of platinum electrodes, the e.m.f. is augmented. E. Müller and W. Stein studied the electrometric titration of palladous chloride with stannous salts, titanic chloride, iodides, and cyanides. F. Müller observed some anomalies in the e.m.f. in hydrochloric acid. C. Drucker studied the diffusion electrodes of palladium. E. Beutel and A. Kutzelnigg obtained anodic films of sulphide by the electrolysis of thiosulphate soln. A. Simek found that drops of molten tellurium dioxide on the surface of hot palladium do not move as when on platinum.

The **electrodeposition** of palladium was discussed by R. W. Harbison,[15] and C. W. Keitel and H. E. Zschiegner. C. W. Keitel prepared a bath with a 10 per cent. soln. of ammonium sulphate or nitrate, containing 5 per cent. of free ammonia, and 2 per cent. of palladous diamminonitrate, replenishing the ammonia and nitrate from time to time. The bath is operated at 95° with 2·2 volts. H. E. Zschiegner used a bath made by boiling palladous chloride with sodium nitrite until the soln. is colourless or pale yellow, and then adding an excess of ammonia. S. Cowper-Coles recommended for the deposition of palladium in a bright form, a 0·62 per cent. of ammonium chloropalladite, dissolved in a 1 per cent. soln. of ammonium chloride. The soln. is maintained at a temp. of about 24°, the current used per square foot being about 0·13 amp., and the e.m.f. at the terminals of the bath 4 to 5 volts. According to R. Amberg, palladium begins to be deposited from an acidic soln. of the chloride at 0·65 volt, but after a short time palladium peroxide comes down on the anode, the voltage rises to about 1·25, and spongy metal is deposited at the cathode. The same difficulties were encountered when alkaline or ammoniacal soln. were used. When an anode rotating some 600 to 650 times per minute is used, however, no peroxide is formed, even with higher currents. The temp. is best kept at 60° to 65° and the voltage must not exceed the critical value of 1·25 volts. R. H. Atkinson and A. R. Raper, P. Haas, P. K. Frölich and G. L. Clark, A. Wogrinz, G. Grube and D. Beischer, V. Kohlschütter and F. Jakober, A. F. Raper, E. F. Smith, W. C. Heraeus, A. Bertrand, I. I. Tschukoff, and M. Frantz studied the subject; H. S. Booth and M. Merlub-Sobel, the deposition from liquid ammonia; and R. H. Atkinson, from soln. in fused alkali chlorides.

According to F. Müller and A. Riefkohl,[16] the electrochemical behaviour of palladium in soln. containing Cl′- and H$^{\cdot}$-ions, of not too high p_H, is quite different from that of the other metals of the platinum group. By passing chlorine into the soln., or by anodic polarization, the metal first dissolves quantitatively at relatively low potentials, but becomes suddenly passive on reaching a certain critical current density. The effect of increasing the conc. of the added hydrochloric acid is to cause complete passivity to occur at higher potentials, and in pure concentrated hydrochloric acid the metal remains active up to very high current densities. Palladium differs from other base metals, such as iron and nickel, in that it remains

completely passive, like platinum, on anodic polarization in soln. free from chloride, whereas iron and nickel in, *e.g.*, sulphuric acid are at first active, and become passive only at higher current densities. Polarization also renders a palladium anode active in soln. containing bromine and chlorine ions. In the transition from the active to the passive condition, characteristic pulsations sometimes occur. These are most marked in the case of iodide soln., but are also sometimes observed in chloride soln. The observed phenomena are discussed by F. Müller and co-workers, and it is suggested provisionally that they may be ascribed to the formation of a sparingly-soluble film of unknown nature on the surface of the electrode. E. Liebreich and W. Wiederholt, A. Thiel and W. Hammerschmidt, F. Meunier, A. Smits, and P. S. Tutundzic studied the overvoltage of hydrogen. G. Tammann and J. Schneider noted that the rate of growth of the oxide film in the anodic polarization of palladium in $1\cdot6N$-H_2SO_4 follows an exponential curve. J. A. V. Butler and G. Drever observed that when electrodes of palladium are anodically polarized in acidic or alkaline soln., an adsorbed layer of oxygen is formed prior to the establishment of the oxygen overvoltage. There is a second stage in the oxidation where oxides of a peroxidic character are slowly formed, and they are reduced cathodically at a more positive potential than the adsorbed oxygen. S. Koidzami, J. A. V. Butler and co-workers, K. R. Koch, and F. Jirsa discussed the anodic polarization of palladium.

C. E. Mendenhall and L. R. Ingersoll[17] observed that small globules of molten metal in Nernst's filament move with the current. R. H. Atkinson studied the electrolytic transfer of palladium using fused chlorides as electrolytes; R. von D. Wegner, the contact electricity; and O. Scarpa, the resistance at the contact surface of electrolyte and electrode.

B. Neumann[18] gave $-1\cdot066$ volt for the **electrode potential** of palladium in a normal soln. of the chloride. P. Nylen studied the effect with palladium black. A. König constructed a hydrogen-palladium diffusion electrode in a cell comprising a horse-shoe-shaped, thin-walled palladium tube immersed in a palladium dish, perforated at the bottom, and filled with a eutectic mixture of potassium and sodium nitrites; hydrogen was passed through the palladium tube, and oxygen through the bottom of the dish, which was covered with spongy palladium to break up bubbles and prevent spurting. At 250°, this cell had an e.m.f. of 0·75 volt when no current was taken from it; with increasing current density at the H_2-Pd electrode, the voltage fell. The optimum current was 0·7 amp. per sq. dm. at 0·5 volt over prolonged periods. C. Drucker, and P. Nylen studied the subject; M. Knobel, and C. A. Knorr and E. Schwartz, the over-voltage of hydrogen on palladium; J. A. V. Butler and co-workers, the oxidation potentials; R. H. Atkinson studied the electrolytic transfer of palladium. F. Jirsa measured the relation between the current density and the potential of a palladium anode against a normal hydrogen anode in N-NaOH at 18°, and inferred that palladium may exist in at least two active states, in addition to the usual passive form. An electrode which has previously been heated in air is always passive. By comparing the potentials at which breaks occur in the current density-polarization curves with those in the corresponding curves for the anodic and cathodic treatment of palladium coated with PdO and PdO_2, respectively, it is concluded that in alkaline soln. a palladium anode is oxidized in the following steps; to Pd_2O (at $+0\cdot15$ volt); to PdO (at$+0\cdot4$ to $0\cdot5$ volt); to PdO_2 (at$+0\cdot95$ volt); and to unstable PdO_3 at 1·22 volts. Oxygen evolution occurs at more positive potentials through the medium of PdO_3, which breaks down into PdO_2 and oxygen. H. Fricke, M. Andauer, and P. S. Tutundzic studied the electrolytic polarization of palladium-black charged with hydrogen with a soln. of sulphuric acid; G. Tammann, the effect of cold-work; and I. Slendyk and P. Herasymenko, the separation of hydrogen at a palladium cathode. J. C. Andrews found palladium electrodes to be less reliable than platinum electrodes in determinations of the conc. of $H^{\cdot}$-ions, because amorphous palladium undergoes a more or less rapid change to the

crystalline state. N. Kobozeff and N. I. Nekrassoff studied the emission of electrons during the cathodic polarization of palladium.

The rate of cathodic spluttering is 100 when that of platinum is 40. K. Meyer and A. G. Schulze,[19] M. A. Rewutzka, H. P. Waran, L. Tonks, and R. K. Cowsik, studied the **cathodic spluttering** of palladium.

The **thermoelectric force** of palladium against platinum was found by L. Holborn and A. L. Day,[20] R. von D. Wegner, and W. Jäger and H. Diesselhorst to be $E=-0{\cdot}56$ millivolt at 100°; J. Dewar and J. A. Flemming gave $-0{\cdot}48$ millivolt; and E. Wagner, $-0{\cdot}30$. The negative sign here means that the current flows from the platinum to the palladium at the cold junction. L. Holborn and A. L. Day gave:

	−185°	−80°	0°	100°	300°	500°	700°	900°	1100°	1300°	1500°
E .	0·77	0·39	0	−0·57	−1·99	−3·84	−6·41	−9·72	−13·70	−18·12	−22·74

J. Monheim studied the palladium-copper couple. W. Jäger and H. Diesselhorst observed for the palladium-iron couple, when the current at the hot junction flows from the palladium to the iron, that the e.m.f. at 13° is 23·7 millivolts per degree, and at 95°, 23·2 millivolts per degree; with the palladium-constantan couple, where the current flows from the constantan to the palladium at the hot junction, the e.m.f. at 13° is 29·3 millivolts per degree, and at 95°, 32·7 millivolts per degree. E. Cohn, and E. Wagner studied the effect of press. on the thermoelectric force; and G. Tammann, and G. Tammann and G. Bandel, the effect of cold-work. The palladium and hydrogenized palladium couple was studied by F. Heinburg, P. Raethjen, R. Nübel, R. M. Holmes, and others—*vide infra*, hydrogenized palladium. F. Rumpf studied the e.m.f. developed in a homogeneous conductor by a fall of temp. in one part. G. Borelius and co-workers studied the thermoelectric force against a silver-gold alloy at low temp. P. W. Bridgman gave for the thermoelectric force, E, against lead, $E=-0{\cdot}0_5 5496\theta-0{\cdot}0_7 1760\theta^2$ volt; for the **Peltier effect**, $P=(-5{\cdot}496-0{\cdot}0352\theta)(\theta+273)\times10^{-6}$ volt; and for the **Thomson effect**, $\sigma=-0{\cdot}0352(\theta+273)\times10^{-6}$ volt per degree. The thermoelectric force with a couple of uncompressed metal and metal compressed at p kgrms. per sq. cm., $E\times10^6$ volts, is:

		10°	20°	40°	60°	80°	100°
$E\times10^6$	2,000p .	0·44	0·88	1·75	2·63	3·50	4·38
	6,000p .	1·28	2·57	5·18	7·85	10·56	13·31
	12,000p .	2·53	5·09	10·32	15·64	21·04	26·52

The Peltier effect between the uncompressed and the metal compressed at p kgrms. per sq. cm., is $P\times10^6$ joules per coulomb:

		10°	20°	40°	60°	80°	100°
$P\times10^6$	2,000p .	12·0	12·9	13·8	14·6	15·5	16·4
	6,000p .	34·9	38·1	41·4	44·6	48·2	51·7
	12,000p .	68·5	75·3	82·4	89·0	96·0	103·4

The Thomson effect, $\sigma\times10^8$ joules per coulomb per degree, is:

		10°	20°	40°	60°	80°	100°
$\sigma\times10^8$	2,000p .	0	0	0	0	0	0
	6,000p .	3·0	3·2	3·4	3·7	3·9	4·1
	12,000p .	9·3	9·4	9·1	9·0	8·5	8·2

E. H. Hall made observations on the subject.

E. H. Hall[21] gave for **Hall's effect** with palladium saturated with hydrogen, in a field of 9000 gauss, $-0{\cdot}0_3 845$ at 26°, and $-0{\cdot}0_3 855$ at 45°; A. von Ettingshausen and W. Nernst gave $-0{\cdot}001150$ at 20° and 5800 gauss; H. K. Onnes and B. Beckman, $-0{\cdot}001385$ at $-258{\cdot}5°$, 0·001368 at $-252{\cdot}7°$, and 0·000675 at 17°; H. Zahn, $-0{\cdot}001112$ to 0·000691 at 18°; and J. Königsberger and G. Gottstein, $-0{\cdot}000680$ at 18°; and for thin films E. H. Hall gave $-0{\cdot}000844$ at 64°; and H. B. Peacock, $-0{\cdot}000570$ at 18°. Observations were made by P. Raethjen, and M. Cantone and E. Bossa; and the effect of the hydrogenization of the palladium

by W. Kaufmann and P. Raethjen. For **Ettinghausen's effect,** E. H. Hall gave $16{\cdot}2\times10^{-9}$ at 26°, and $18{\cdot}8\times10^{-9}$ at 45° for palladium saturated with hydrogen, and for thin films, $20{\cdot}6\times10^{-9}$ at 64°. For **Nernst's effect,** with hydrogenized palladium, H. Zahn gave $0{\cdot}0_451$ to $0{\cdot}0_3127$ at 18°; E. H. Hall, 0·000327 at 25°, and 0·000326 at 45°; and for thin films of palladium, 0·000335 at 67°. For **Leduc's effect,** with hydrogenized palladium, H. Zahn gave -18×10^{-9} to -33×10^{-9} at 18°; and E. H. Hall gave $-48{\cdot}7\times10^{-9}$ at 25°, and $-41{\cdot}4\times10^{-9}$ at 45°; and for thin films of palladium, $-37{\cdot}8\times10^{-9}$ at 67°.

M. Faraday [22] made some observations on the magnetic properties of palladium. The metal is paramagnetic. W. Finke gave 66×10^{-6} mass unit; and Y. Shimizu, $5{\cdot}20\times10^{-6}$ mass unit for the **magnetic susceptibility** at room temp.; W. Kopp gave $5{\cdot}269\times10^{-6}$ mass unit at 17·1°; P. Curie, $5{\cdot}2\times10^{-6}$ mass unit at 14°; K. Honda gave $5{\cdot}8\times10^{-6}$ mass unit at 18°, and $2{\cdot}0\times10^{-6}$ at 1100°. J. Königsberger gave 50×10^{-6} to 60×10^{-6} vol. unit, and W. Finke, $66{\cdot}26\times10^{-6}$ vol. unit. A. E. Oxley gave for the magnetic susceptibility of platinum black $6{\cdot}43\times10^{-6}$ mass unit at room temp. B. Cabrera and A. Dupérier, and N. F. Mott studied the subject. A. N. Guthrie and L. T. Bourland found that the magnetic susceptibility follows the Curie-Weiss rule up to 427°, and the deviations are attributed to an underlying diamagnetism independent of temp. E. Vogt, R. B. Jones, J. Aharoni, F. H. Loring, and E. C. Wiersma studied the subject; and G. Tammann, and K. Honda and Y. Shimizu, the effect of cold-work; C. Sadron, A. N. Guthrie and M. J. Copley, and P. Weiss studied the magnetic moment; P. Weiss and G. Foex, the atomic moments. For the effect of hydrogen, *vide infra,* hydrogenized palladium.

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§ 4. The Chemical Properties of Palladium

W. Ramsay,[1] and W. A. Tilden observed that palladium does not absorb **helium,** but greedily absorbs hydrogen, and hence W. Ramsay and co-workers were able to separate hydrogen from admixed helium. F. Paneth and K. Peters found palladium almost impermeable to helium at all temp. investigated. A. Sieverts and E. Bergner could detect no absorption of helium by palladium at 1400° to 1600°, but M. E. Klarmann said that helium is absorbed by activated palladium. F. Fischer and co-workers observed no evidence of chemical combination when palladium is electrically spluttered under liquid **argon.** M. E. Klarmann said that activated palladium absorbs 319 times its vol. of argon ; and 446 times its vol. of **neon.** At the same time, the electrical resistance increases, respectively, by 24 and 33 per cent. The subject was studied by V. Kohlschütter. W. Ramsay and M. W. Travers observed that argon does not diffuse through red-hot palladium.

Compact palladium, spongy palladium, palladium black, or colloidal palladium all absorb or occlude **hydrogen.** The proportion of gas absorbed in some cases depends on the physical state of the metal. L. P. Cailletet and E. Colardeau, and others observed that in the electrolysis of acidulated water with a platinum anode, and a palladium cathode, oxygen is evolved at the anode, but no hydrogen appears at the cathode until the metal is saturated with gas when hydrogen is evolved as

the electrolysis proceeds. If the current is passed through electrodes of spongy palladium and dil. sulphuric acid, until both electrodes are saturated with gases, and the two electrodes then placed in electrical communication, a kind of gas battery is formed. Under atm. press. the discharge lasts about 10 seconds, and the e.m.f. falls to zero. The duration of the current is increased by press. The subject was discussed by M. Berthelot. M. Thoma observed that the palladium may be supersaturated with hydrogen during the electrolysis, and the excess of gas is evolved when the passage of the current ceases. J. C. Poggendorff, J. L. Smith, T. Wilm, R. Böttger, F. Wöhler, H. Schiff, J. Dewar, W. Odling, and G. S. Newth devised experiments to illustrate the expansion which occurs when the palladium is hydrogenized. For instance, if electrode plates of palladium are varnished on one side, as the acidulated water is electrolyzed, the palladium cathode curls with the varnished side inwards as hydrogen is absorbed, but the anode remains straight. On reversing the current the curled plate becomes straight, and the straight plate curled. The phenomenon is connected with the increase in vol. which occurs when hydrogen is absorbed by the metal. A. Coehn and K. Sperling followed the motion of hydrogen in palladium by the action of the metal on hydrogen dioxide. A. Sieverts and G. Zapf, and H. W. Melville and E. K. Rideal compared the absorption of hydrogen and deuterium by palladium.

T. Graham observed that at ordinary temp. palladium absorbs 376 vols. of hydrogen, without altering its general appearance. Palladium which has been ignited in vacuo absorbs the gas copiously at ordinary temp.; the gas is absorbed —rapidly at first and subsequently more slowly—and the hydrogenized palladium gives off a large proportion of the absorbed gas when it is placed in vacuo; and it loses hydrogen slowly when it is exposed to the atmosphere; the gas is rapidly and almost completely evolved at 100° in vacuo. When the metal is heated in hydrogen, and allowed to cool in the gas, it absorbs up to 935 times its vol. of hydrogen. G. Neumann and F. Streintz gave the relative capacities for the occlusion of hydrogen by palladium black, platinum sponge, etc.:

Pd	Pt	Au	Fe	Ni	Cu	A	Pb
502	49·3	46·3	19·2	17·6	4·5	2·7	0·15

A. Sieverts found that less hydrogen is absorbed by molten palladium so that no spitting occurs when the molten metal solidifies in hydrogen. C. Paal and J. Gerum observed that palladium hydrosol absorbs 2952 vols. of hydrogen per vol. of metal; and C. Paal and C. Amberger were thus able to convert colloidal palladium into *colloidal* hydrogenized palladium. A. Sieverts measured the equilibrium conditions of the occluded hydrogen at different temp. and press. with compact palladium. The results, summarized in Fig. 5, represent the effect of temp. on the absorption of hydrogen by 100 grms. of compact palladium at atm. press., and at different temp. The ordinates in vols. of hydrogen absorbed by the commercial metal are indicated in brackets. The impure metal does not absorb so much gas as the purified metal, and this the more, the lower the temp. As in the case of tantalum, but unlike other metals, the proportion of dissolved hydrogen decreases with temp. Specimens of palladium in which the surface area per unit mass varies considerably have the same absorptive power; so that the quantity of absorbed hydrogen per unit mass is independent of the surface, in agreement with the assumption that the process of absorption is a true dissolution. Under similar conditions spongy palladium and compact platinum occlude nearly the

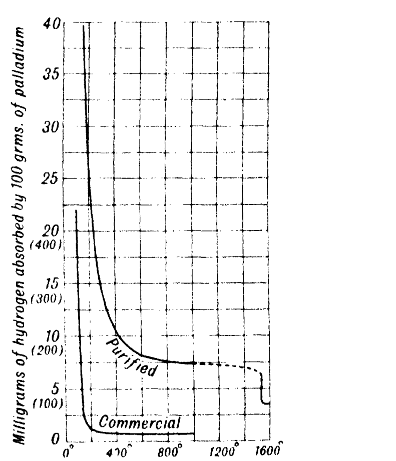

FIG. 5.—The Absorption of Hydrogen by Palladium at Different Temperatures.

same proportion of hydrogen, but platinum black between 140° and 440° absorbs more hydrogen than is the case with compact platinum, although L. Mond and co-workers found the absorptive power to be independent of the state of the metal. The power of absorption by palladium black is lowered, and approximates more to that of the compact metal. There are also some undetermined influences which affect the absorptive power of palladium black—notably the mode of preparation; and M. I. Temkon and A. N. Bakh found the adsorption was not affected by the presence of water or oxygen. G. Kernot and F. de S. Niquesa noted that colloidal palladium absorbs more hydrogen than is the case with the metal in any other physical state. The absorption is diminished if the colloidal soln. contains gum, dextrin, or albumen, but it is not sensibly influenced by sugar. V. Lombard and C. Eichner, and W. Jost and A. Widmann compared the results with the different isotopes of hydrogen; and G. Tammann and J. Schneider discussed the relationship between the crystal structure and the rate of adsorption by metals. H. O. von Samson-Himmelstjerna studied the electrolytic charging of palladium with hydrogen; W. W. Hurst and F. K. Rideal, the promotor action of palladium in the adsorption of hydrogen by copper. T. Sabalitschka studied the effect of different carriers of palladium on the adsorption. A. Gutbier and co-workers, and C. Paal and C. Amberger found that the absorption increases with a fall of temp. down to −50°, and there is a minimum at about 20°. These results do not agree with those of A. de Hemptinne, and H. Baerwald.

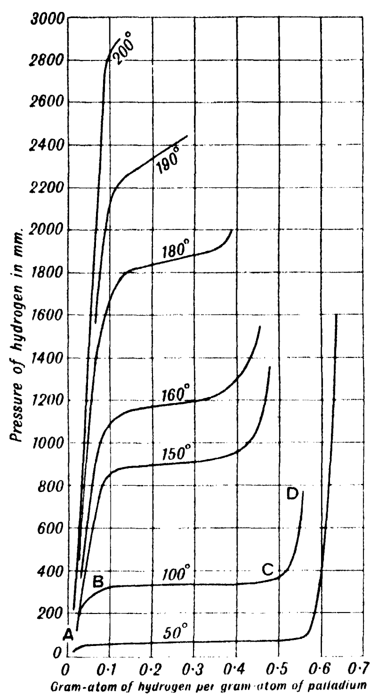

FIG. 6.—The Effect of Pressure on the Solubility of Hydrogen.

The relation between the absorptive power and temp. observed by A. Sieverts was also studied by L. Troost and P. Hautefeuille, H. S. Taylor and R. M. Burns, A. Gutbier and co-workers, H. B. Roozeboom, and by C. Hoitsema. The gaseous press. corresponding with definite concentrations of the hydrogen occluded in palladium were measured. If the absorbed hydrogen forms a compound with the metal, then by reducing the vol. of hydrogen in contact with the palladium, no increase of press. should be observed but only an increase in the amount of compound formed. C. Hoitsema's curves at different temp. are shown in Fig. 6. There is first a rise of press. as the proportion of hydrogen increases, there is then a stationary period where the press. remains constant even though the proportion of absorbed hydrogen increases, and thereafter, an increase of press. with an increase in concentration of absorbed hydrogen. L. Troost and P. Hautefeuille thought that the flattening of the curve showed that **palladium hemihydride** was formed, Pd_2H, but the length of the central position of the curves diminishes with rise of temp., and it does not end at the same conc. of hydrogen in each case. This is taken to favour the hypothesis that the hydrogen is dissolved in, and not chemically combined with, the metal. T. Graham also favoured the assumption that the occluded hydrogen is present in the physical condition of a liquid, and acts as a quasi-metal to form a kind of alloy analogous to the amalgams. The subject was studied by J. Hagenacker, V. V. Ipatéeff and V. G. Troneff, W. Beetz, G. Tammann, J. B. Firth, C. J. Smithells, G. Wolf, G. Neumann and F. Streintz, F. Halla, A. Berliner, M. A. Schirmann, and G. Borelius. Owing to the effect of the occluded

hydrogen on the physical properties of the palladium, T. Graham called the occluded hydrogen hydrogenium, and he calculated its sp. gr. to be 0·733; J. Dewar gave 0·620, which is equivalent to the condensation of 7 litres of gas into a space of 1 c.c. E. Müller and K. Schwabe observed that of the hydrogen taken up by reduced palladium 2·6 to 14·4 is absorbed irreversibly (chemical combination), and the remainder reversibly (dissolution), or molecular penetration in the space-lattice. The subject was discussed by G. Rosenhall.

C. Hoitsema's curves thus represent two solid phases in contact with a gas phase, the press. of which can change considerably without provoking rapid changes in the solids. According to the phase rule, at a given temp. two solid phases cannot be in equilibrium with gas at more than one press. A. Sieverts observed that at a constant temp., the amount of hydrogen, S, absorbed depended on the press., p, between 1 and 760 atm., such that $S=k_1p^{\frac{1}{2}}\times k_2p$, where k_1 and k_2 are constants. The result is taken to mean that hydrogen molecules are in equilibrium with hydrogen atoms both in soln. in the palladium, and in the gaseous phase, and that Henry's law—**1**. 10, 4—holds for the gas in both the molecular and the atomic condition. High press. favour the H_2-molecule, low press. favour at. hydrogen. C. Hoitsema assumed that the ascending part of the curve AB represents the press. of one solid soln., say α, and the part CD, the press. of the other solid soln., say β, whilst the flattened portion of the curve represents the joint press. of both solid soln. With increasing proportions of hydrogen, the α-solid soln. is being converted with the β-solid soln. The miscibility of the solid soln. is very small at low temp.; and the narrowing of the flattened portions of the curves with rise of temp. corresponds with the increasing miscibility of the two solid soln. with rise of temp. H. Jellinek studied the action of hydrogen, at high pressures, on palladium.

According to A. R. Ubbelohde, and A. R. Ubbelohde and A. Egerton, the flattening of the curve is not satisfactorily explained by the hypothesis of C. Hoitsema, or of J. H. Andrews and A. Holt, and they explain the flattening of the curve by the following kinetic hypothesis:

Palladium, like other transitional elements, adsorbs hydrogen on its surface. The adsorption is not very large, and may be assumed to be proportional to the press. If the number of active points on the surface is z, the fraction occupied will be bpz, where b is constant at constant temp. The rate of entry into the lattice will be $bdpz$, where d is a constant at constant temp. (d involves the energy necessary for the activation of the reaction $H_2 \rightarrow 2H$). The rate of loss of hydrogen from the lattice near the surface depends *inter alia* upon the rate of diffusion of the atoms, but if the rate of loss is small compared with the rate at which fresh atoms can travel to the surface, the rate of loss will be practically independent of the conc. of hydrogen in the solid phase; we may write it fz, where f is nearly constant at constant temp. At equilibrium, $bdzp=fz$, that is, $p=$constant. Thus a flat part will be obtained as long as the velocity of diffusion of the hydrogen atoms or protons is more than sufficient to supply the rate of loss. As the conc. in the solid phase diminishes, a region is reached where this no longer holds, and the rate of loss depends upon the conc. in the solid phase. A third branch of the isothermal, beyond the point Pd_2H, may be due to surface adsorption only, or to the additional hydrogen in the lattice leaving it by another mechanism.

J. Dewar's values for the effect of press. up to 120 atm. between 360° and 500°, agree with A. Sieverts' formula—300 vols. were absorbed by compact palladium at 360° and at 60 atm. press., or at 500° and 120 atm. press. S. Valentiner studied the effect of low temp. and low press., p mm., on the absorption of hydrogen expressed in milligrams per gram of metal, and the results are summarized in Fig. 7. He concluded that some of the hydrogen is adsorbed on the surface, and some is dissolved by the metal. Observations on the occlusion of hydrogen were made by F. Müller, I. I. Zukoff, J. Zeutschel, D. P. Smith, A. Bartsch, and

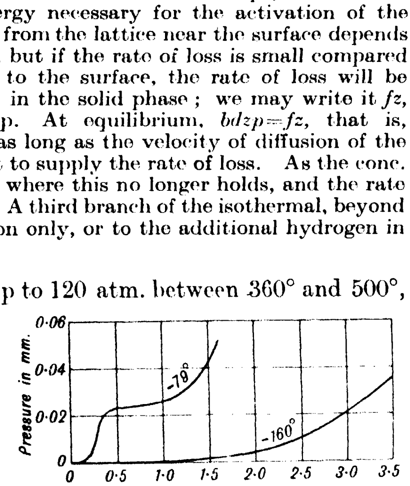

Fig. 7.—The Effect of Pressure on the Absorption of Hydrogen.

A. Puodziukynas. When hydrogen is added to palladium there is a rapid transference of a relatively large proportion of hydrogen from the gaseous to the solid phase, and this is followed by a subsequent, and much smaller, proportion of gas from the gaseous to the solid phase. These phenomena have been attributed to a rapid condensation, or adsorption of gas molecules on the surface of the solid, followed by a much slower process of diffusion of the adsorbed gas into the interior of the solid-absorption. W. Krause and L. Kahlenberg measured the speed of hydrogenation of palladium.

B. Lambert and S. F. Gates measured the pressure-concentration equilibria at 75°, 103°, and 120°. Different curves were obtained by approaching the equilibrium by adding and by removing hydrogen—in the latter case, the equilibrium press. is lower than it is in the former case; and if the temp. of the system in equilibrium is allowed to fall to the temp. of the room for some hours and then allowed to return to the original value, the equilibrium press. is reduced, and does not rise to its original value. The horizontal portions of descending isothermals all begin at a conc. approximately Pd_2H, and this favours the assumption that a hemihydride is formed since it is not likely that the break would occur at a fixed point of a solid soln., or two immiscible solid soln. would be formed at temp. as wide apart at 75°, 103°, and 130°. G. Borelius, G. Tammann, B. Duhm, F. J. Tromp and B. de Loor, and V. V. Ipatéeff and V. G. Troneff studied the subject. M. H. Hey investigated the dissociation pressure of the palladium-hydrogen system on the assumption that there is only one limiting phase, PdH.

A. Holt and co-workers observed that the curve representing the rate of soln. of hydrogen in compact palladium at constant press., and the conc. of the gas in the metal consists of two distinct portions, and it is assumed that this indicates that two modifications of the metal are present. The first portion of the curve represents the rapid dissolution of the gas in active or α-palladium, and the second portion of the curve represents the dissolution of the gas in inactive or β-palladium. The curve obtained with palladium black is continuous, showing that it consists almost entirely of α-palladium. Both varieties of palladium cease to absorb hydrogen above a certain temp., and above 150°, they both have an equal capacity for the absorption of hydrogen. F. Halla assumed that palladium exists in dimorphic forms with a transition point at 150°. J. B. Firth showed that below 0°, hydrogen is wholly adsorbed by palladium, and above 150°, it is wholly absorbed. B. Lambert and S. F. Gates also found that their results are consistent with the dimorphism of palladium; and A. Sieverts showed that palladium black passes into palladium sponge when ignited, and there is a simultaneous increase in the amount of hydrogen absorbed at temp. below 600°. Above this temp., the absorption of hydrogen by all varieties of palladium is virtually the same. The two forms of palladium are the crystalline and the amorphous; the amorphous has a greater absorptive power than the crystalline form. Heating the palladium alters the relative proportions of these two forms and at the same time alters their capacity for absorption. A. Sieverts suggested that the sorption of hydrogen by amorphous palladium is a case of adsorption, and by the crystalline variety, absorption. J. Schneider studied the effect of crystal orientation on the rate of absorption of hydrogen by palladium.

L. J. Gillespie and F. P. Hall observed that the pressure-concentration curves of the Pd-H system indicate the existence of two solid soln.; the saturated one, richer in hydrogen, has approximately the composition of the hemihydride Pd_2H at 80°, 160°, and 180°, but contains larger proportions of hydrogen at lower temp., 0° and 30°. Consequently, it is assumed that the hemihydride has a definite existence at the higher temp. L. J. Gillespie and J. H. Perry observed an extension of the pressure-concentration curve at 0° into the metastable region. The C-bend, Fig. 6, for the curves between 80° and 180° corresponds with the hemihydride. Equilibrium was not attained in the measurements of L. Troost and P. Hautefeuille, and C. Hoitsema. J. O. Linde and G. Borelius showed that the X-radiograms of

the system at 100°, and 150°, and 200°, at press. between 0·1 and 4·0 atm., indicate the existence of two phases : a soln. of hydrogen in palladium with Pd : H>1 : 0·5, and with the lattice constant 3·88 to 3·92 A. ; and palladium hemihydride with a lattice constant a=3·978 A. There are indications of two crystalline forms of the hemihydride, Pd_2H ; and also of a third phase, a continuation of the first phase, but with Pd : H<1 : 0·5, and which corresponds with the phase very rich in hydrogen obtained by T. Graham by electrolysis—*vide supra*. It is also possible that the hydrogen in the palladium lattice is present in the atomic state, and to be accommodated in the interstices of the metal lattice—*vide infra*.

T. Graham observed that hydrogen readily diffuses through palladium at temp. exceeding 240°. No gas appeared to pass through the walls of a palladium tube in an atm. of hydrogen at 100° ; and hydrogen began to pass through at 240°, and at 265° it passed through a 1 mm. wall at the rate of 327 c.c. per sq. metre per minute, and just below redness, near 500°, the rate increased to 423 c.c. per sq. metre per minute. With coal gas in place of hydrogen, penetration by hydrogen, but not by hydrocarbons, began at about 240°. The subject was studied by W. Ramsay, B. Duhm, and M. Thoma. W. Jost and A. Widman found that H^2 differs more slowly than H^1. The phenomena suggest a mode of separating hydrogen from hydrocarbons. The press. of the hydrogen within the tube is less than the press. of the hydrogen outside the tube no matter what inert gas be mixed with the hydrogen ; if p_1 denotes the internal press. and p the external press., then, for equilibrium, W. Ramsay observed p_1/p=0·8984 to 0·9693 ; and D. Tsakalotos, 0·9238. W. Ramsay suggested that the molecules of hydrogen are split or dissociated into atoms in their passage through hydrogen, and C. Hoitsema came to the same conclusion for temp. exceeding 100°—*vide supra*. E. Bose also assumed from his observations on gas cells that the hydrogen occluded in platinum is in the atomic state. S. Guggenheimer did not detect any evidence of ionization in the gas liberated from hydrogenized palladium at 200° ; and P. Anderson could detect no evidence of the ionization of hydrogen, as evidenced by its electrical conductivity, by contact with palladium or palladium black. Both P. Anderson, and Y. Venkataramaiah and M. V. N. Swamy noted that hydrogen after it has passed over palladium black, or diffused through palladium, can reduce sulphur to hydrogen sulphide at ordinary temp. E. B. Maxted, and L. W. McKeehan noted that hydrogen sulphide hinders the absorption of hydrogen owing to the formation of a film of palladium sulphide ; and M. V. Poljakoff observed a luminescence in cooled hydrogen which has been passed over a hot palladium plate. A. Coehn found that diffusion experiments support the view that hydrogen forms electrons and protons in passing through palladium. A. de Hemptinne showed that palladium which has once been employed as an absorbent for carbon monoxide loses the faculty of absorbing hydrogen at a low temp. M. Bourguel and V. Grédy discussed the theory of the catalysis ; W. Hempel, A. D. Tschirikoff, and C. Paal and C. Amberger employed the hydrogenized palladium in gas analysis.

A. Winklemann employed the hypothesis that the atoms, not molecules, of hydrogen pass through palladium at high temp. because he found that the quantity of hydrogen which passes through a palladium septum does not diminish proportionally with the press. Assuming that the hydrogen dissociates into atoms, and that the quantity of gas, [H], diffusing in the metal is proportional to the press. of the dissociated mols., p_1, when the press. of the undissociated mols. is p, he represented the quantity of hydrogen which diffuses in unit time at a total press. P, is $[H]=a\sqrt{KP}\{(1+K/4P)^{\frac{1}{2}}(K/4P)^{\frac{1}{2}}\}$, where $K=p_1{}^2/p$, and a is a constant. With the same fundamental assumption, O. W. Richardson obtained the expression $[H]=a(\sqrt{PT}/h)e^{-b}/T$, where a and b are constant, for the quantity of hydrogen diffusing through the metal through a plate h cm. thick, at a press. P and the absolute temp. T, per second. The measurements of A. Holt and co-workers—*vide supra*—showed that the rate of diffusion is proportional to the press. of the gas, but below 100 mm., the rate of diffusion is slower than corresponds with this

simple proportion, and it is not related with any simple function of the press. G. N. S. Schmidt found that the rate of diffusion increases very much as the temp. rises from 160° to 300°. V. Lombard and C. Eichner found that the rate of diffusion, at 770 mm., varies linearly with temp. between 400° and 600°; and at 372°, for press. between 40 and 770 mm., the rate of diffusion is proportional to $p^{0\cdot 8}$. L. Harris and co-workers studied the separation of the isotopes of hydrogen by diffusion through palladium. C. Wagner observed that the change in the concentration of hydrogen, C, with time, t, is dependent on the press. of the hydrogen, p_{H_2}, and there are two definite phenomena involved, $dC/dt, =k^1\sqrt{p_{H_2}}-kC$, or $dC/dt=k(C_e-C)$, where C_e denotes the concentration of hydrogen for equilibrium at a press., p_{H_2}. This equation is valid for the reaction $H_{2gas}\rightleftharpoons 2H_{dissolved}$, and it was also worked out by E. Jurisch. C. Wagner also observed that for the reaction $H_{2adsorbed}\rightleftharpoons 2H_{dissolved}$, the velocity equation is $dC/dt=k_1p_{H_2}-k_2C_2$, or $dC/dt=k_2(C_e^2-C^2)$. A. Coehn and W. Specht found that the resistance of a palladium wire is independent of the distribution of hydrogen within it, and it gives a good measure of the hydrogen content. The hydrogen moves towards the negative pole, and the velocity of this motion is dependent on the temp. Observations were also made by S. Guggenheimer, V. Lombard and C. Eichner, A. Coehn and H. Baumgarten, A. Lessing, H. Dünwald and C. Wagner, H. Hulubei, K. Lisenko, N. I. Kobozeff and V. Monblanova, S. Makareva, and A. L. Ferguson and G. Dubpernell. V. Lombard and C. Eichner compared the rate of diffusion of the two isotopes of hydrogen.

G. Harker found that X-rays and γ-radiations stimulate the catalytic activity of palladium in the hydrogenation of ethylene. M. Yamada, and G. Tammann examined the X-radiograms of hydrogenized palladium, and concluded that the adsorbed gas is in solid soln. with hydrogen atoms in the interspaces of the palladium lattice. This produces an expansion of the space-lattice. L. W. McKeehan observed an expansion in the lattice parameter from $a=3\cdot 900$ A. to $a=4\cdot 039$ A. when the absorbed hydrogen amounts to that required for Pd_2H. A. Osawa observed a 2·8 per cent. expansion of the lattice parameter, when palladium is saturated with hydrogen. J. O. Linde and G. Borelius found that the lattice constant of palladium is $a=3\cdot 888$ A.; when the absorbed hydrogen is less than is required for Pd_2H, $a=3\cdot 888$ to 3·920 A.; and when the amount absorbed is just that required for Pd_2H, $a=3\cdot 978$—*vide supra*. J. D. Hanawalt found that the palladium lattice is distorted by hydrogen owing to the formation of a hydride, Pd_2H. The results indicate that in hydrogenized palladium there is a lattice due to palladium alone superposed on one due to the hydride. G. Rosenhall, I. I. Tschukoff, G. Tammann, E. Nähring, F. Krüger and G. Gehm, and F. Krüger and E. Nähring studied the subject. T. Graham observed that when palladium absorbs 936 times its vol. of hydrogen, its sp. gr. falls from 12·38 to 11·79; G. Wolf observed that by saturating palladium wire with hydrogen, the sp. gr. fell from 11·78 to 10·07 in one case and to 10·447 in another case. According to M. Thoma, palladium charged with hydrogen electrolytically, expands and increases in vol. equally in all directions. A contraction takes place on removing the hydrogen, which is greater than the previous expansion, but if the palladium is successively charged and discharged the contraction lessens in amount, not, however, with any definite regularity. Only a certain amount of hydrogen can be permanently retained, for palladium charged with hydrogen beyond a certain limit parts with the gas spontaneously. Below this limit of saturation, the expansion is proportional to the amount of hydrogen absorbed, but on passing the limit the expansion increases more rapidly than the absorption. The hydrogen retained above the limit of saturation is therefore less dense than that retained below. All hydrogen retained above the saturation point is given off when the palladium is left to itself again, and a contraction takes place equal to the expansion due to supersaturation. The supersaturation is dependent in amount very largely on the strength of the electric current employed. G. Wolf observed that the decrease in sp. gr. can be

represented by a curve, Fig. 8, which has a steep, hyperbolic portion followed by a slowly-falling, straight line. O. Feussner observed that the Brinell's hardness increases from 40 to 110 kgrms. per sq. mm. L. W. McKeehan calculated that the sp. gr. of palladium being 11·87, that of Pd_2H is 10·76. T. Graham found that

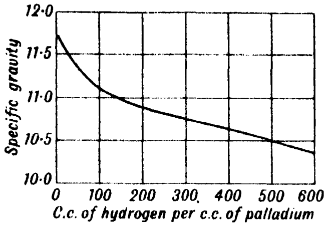

FIG. 8.—The Effect of Occluded Hydrogen on the Specific Gravity of Palladium.

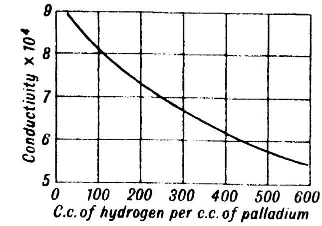

FIG. 9.—The Effect of Occluded Hydrogen on the Conductivity of Palladium.

by saturating palladium wire with hydrogen, the tensile strength fell 81·29 per cent.; and K. R. Koch observed a decrease in the elastic modulus of 21 per cent., and a decrease in the torsion modulus of 16·5 per cent. K. R. Koch, G. Ercolini, and N. Hesehus made some observations on this subject. N. Beketoff studied the heat capacity of the occluded hydrogen; and G. Bethe, the photoelectric properties of the hydrogen. A. Coehn and K. Sperling found that a palladium wire charged with hydrogen affects a photographic plate. According to T. Franzini, when a negative potential of 15,000 volts is applied to a nickel cylindrical plate surrounding a hydrogenated palladium wire in vacuo, the hydrogen is rapidly removed from the palladium. J. Aharoni and F. Simon studied the magnetic properties of the adsorbed gas.

T. Graham observed that much heat is developed during the occlusion of hydrogen by palladium, and that palladium highly charged with hydrogen is pyrophoric. L. Mond and co-workers found the heat of condensation of hydrogen in palladium at about 22°, and 1 atm. press., is near 4644 cals. per gram of hydrogen, or 9362 cals. per mol. of hydrogen. L. J. Gillespie and F. P. Hall gave 8780 cals. per mol. at 0°, 8700 cals. at 30°, and 8450 cals. at 80°; P. A. Favre gave 4514 cals. per gram; and J. Moutier, 4147 cals. per gram. L. J. Gillespie and H. A. Ambrose found that the reaction $4Pd+H_2=2Pd_2H$ at 0° has a thermal value of 9280 cals., and is attended by an increase in internal energy of -8740 cals. A. Sieverts and A. Gotta, and J. Franck studied the subject. J. R. Partington showed that the dissociation press. observed by L. Troost and P. Hautefeuille fit a curve of the type $\log p=AT^{-1}+B$, where A and B are constants; and accordingly, if Q cals. denotes the heat of dissociation $Pd_4H_2=4Pd+H_2$, $4{\cdot}571 \log p=QT^{-1}+$ constant, and $Q=9137$ cals., or 4568 cals. per gram-atom of hydrogen, in agreement with the value 4672 cals. observed by L. Mond and co-workers. This favours the hypothesis that a definite hemihydride is formed. C. G. Fink and co-workers found that H^1 diffuses faster than H^2. R. Nübel discussed the thermal energy of palladium charged with hydrogen. M. Bourguel and co-workers also assumed that a hydride is formed when hydrogen acts on colloidal platinum. W. C. Roberts-Austen and C. R. A. Wright obtained 0·07586 to 0·08463 for the sp. ht. of the occluded hydrogen.

According to H. Brüning and A. Sieverts, A. Coehn and K. Sperling, F. Fischer, T. Graham, H. Hagen and A. Sieverts, E. A. Harding and D. P. Smith, H. Jellinek, M. E. Klarmann, C. A. Knorr and E. Swartz, C. G. Knott, K. R. Koch, A. A. Krakau, F. Krüger and G. Gehm, F. Loessner, W. E. McElfresh, E. Newbery, A. Sieverts, D. P. Smith and co-workers, and T. Sexl, the electrical resistance of palladium steadily increases as the proportion of absorbed hydrogen increases. If [H] denotes the vol. of hydrogen absorbed per unit vol. of metal, the resistance, R, increases in accord with $R=R_0(1{\cdot}0292+0{\cdot}000668[H])$. G. Wolf observed that by

saturating a wire with hydrogen, the electrical conductivity decreased from $9{\cdot}317 \times 10^4$ mhos to $4{\cdot}531 \times 10^4$ mhos. G. Wolf observed that the sp. conductivity curve of palladium can be divided into three parts: (i) with up to 40 vols. of hydrogen per vol. of metal, the conductivity decreases proportionally with increasing conc. of hydrogen ; (ii) with from 40 to 600 vols. of hydrogen, the compound Pd_2H is supposed to be formed, and the conductivity decreases asymptotically ; and (iii) with above 600 vols. of hydrogen to 1 vol. of palladium, the hydrogen dissolves in the hemihydride, and the conductivity falls proportionally with the further amount of hydrogen absorbed. When palladium is made the cathode in the electrolysis of sulphuric acid, the amount of hydrogen absorbed varies with the current density, the time, and the temp. J. O. Linde and G. Borelius observed that as the hydrogen content increases, the system shows two phases at first, followed by a phase exhibiting a lattice constant of 4·034, which rises to 4·07 A. with supersaturation. The relation between lattice constant and hydrogen concentration is approximately linear. The resistance of the palladium-hydrogen system increases regularly up to a concentration $c=0{\cdot}75$H/Pd, and then decreases, the fall being very marked from $c=0{\cdot}85$ onwards ; whence it is concluded that the compound Pd_2H has a relatively small resistance. From the pressure-concentration diagram it is concluded that the system is best envisaged as a metallic mixed-crystal system with the components Pd and PdH. B. Beckman studied the effect of press. J. Shields found that the e.m.f. curves of a cell agreed with the presence of a definite hydride in hydrogenized palladium. R. Nübel, A. Coehn, and T. Sexl discussed the electron theory of the conductivity of hydrogenized palladium. R. Köhler studied the reduction potential. J. Shields found that the e.m.f. of a cell with palladium containing a small and palladium containing a large proportion of occluded hydrogen in dil. sulphuric acid is nearly zero, and does not behave like a true concentration cell as would be the case if the absorption of hydrogen were simply a process of solution. The results agree better with the assumption that a definite chemical compound is formed. M. Wien, and F. Krüger discussed the polarization capacity of hydrogenized palladium. D. P. Smith and F. H. Martin measured the cathode potential of hydrogenized palladium ; and the subject was studied by C. Fromme. M. V. Poljakoff studied the activation of hydrogen by palladium ; and S. Roginsky, the recombination of the atoms of adsorbed hydrogen. C. G. Knott observed that hydrogenized palladium develops a thermoelectric force when coupled with ordinary palladium, and a current flows through the hot junction from the palladium to the hydrogenized metal. There is an e.m.f. of 1·83 millivolts at 100° with a couple containing one wire charged with 692 vols. of hydrogen per vol. of palladium. R. Nübel found the thermoelectric force of palladium against palladium charged with hydrogen is about $1{\cdot}6 \times 10^{-6}$ volt per degree per vol. of hydrogen absorbed—the palladium wire is negative to that of palladium-hydrogen. Observations were also made by L. Kahlenberg, P. Anderson, F. Heimburg, and R. M. Holmes.

T. Graham said that the paramagnetism of palladium is augmented by hydrogenization, but H. F. Biggs observed that palladium containing only a trace of iron, and saturated with hydrogen at the cathode, was almost magnetically neutral. The subject was studied by B. Svensson. A. E. Oxley found that the magnetic susceptibility of palladium black fell 75 per cent.—namely, from $64{\cdot}3 \times 10^{-7}$ to $14{\cdot}7 \times 10^{-7}$ mass unit—when hydrogenized. He said that the hydrogen cannot be in the atomic state, and free, because such a system would be more magnetic than uncharged palladium black ; the hydrogen cannot be in the molecular form condensed to a gas or liquid since there would be only a small decrease in the magnetic property of the system dependent on the minute diamagnetic susceptibility of hydrogen and the amount of gas absorbed ; it is therefore assumed that a compound of hydrogen and palladium is formed with its own specific susceptibility. This compound is taken to be Pd_2H, and if a still greater quantity of hydrogen is occluded, it may form *palladium monohydride*, PdH, or the excess of hydrogen

may form a solid soln. W. Ramsay and co-workers discussed the possibility of the formation of *palladium tritadihydride*, Pd_3H_2. E. Fritzman, B. Svensson, and G. F. Hüttig discussed these alloys; and W. Biltz, their mol. vols.

L. Quennessen said that palladium heated in hydrogen, and subsequently exposed to a current of cold, dry carbon dioxide still retains the property of forming moisture when brought in contact with air. H. W. Underwood, V. S. Sadikoff and A. K. Mikhailoff, T. Kariyone, A. de Hemptinne, O. Schmidt, M. Bourguel, A. A. Alchudzhan and co-workers, P. D. Dobuichin and A. V. Frost, A. V. Frost, J. E. Nyrop, A. S. Ginsberg, and M. Bourguel and V. Grédy studied the catalytic effect of palladium in hydrogenizations; and E. Biilmann and A. Klit, and M. Bourguel, colloidal palladium. M. Bourguel assumed that the palladium takes up hydrogen to form a film Pd_nH_2, which exposes the surface arrangement H.Pd.H to the acceptor of hydrogen. The acceptor is adsorbed at its point of attack, and it evaporates in an activated state in which it can either combine with hydrogen, or suffer de-activation, or stereomutation. G. Bredig and R. Allolio, and C. Sandonnini and G. Quaglia studied the catalytic action on the oxidation of hydrogen in the presence of ethylene, allyl alcohol, and nitrobenzene. L. Vallery studied the poisoning of palladium as a catalyst by stibine and arsine. M. Traube discussed the slow oxidation of hydrogenized palladium. A. Sieverts and K. Brüning studied the adsorption of hydrogen by the palladium-boron alloys.

According to J. R. Bréant,[2] bright palladium acquires a violet film when heated to dull redness in **air**, and if heated for a long time, it acquires a blue tarnish. At a higher temp., the metal recovers its metallic lustre, and retains it if suddenly cooled by quenching in water. W. J. Cock found that at a dull red-heat palladium slowly acquires a friable crust of brown oxide which is reduced to metal at a higher temp. J. J. Berzelius observed that palladium black, obtained by reduction with hydrogen, acquires a blue film on exposure to air, but any increase in weight is too small to be detected by the balance. The blue film is removed by hydrogen gas. D. P. Smith, and A. Coehn discussed the absorption of oxygen by palladium; and A. L. Ferguson and G. Dubpernell, the diffusion of oxygen in the metal; and P. V. McKinney's curve is shown in Fig. 10. R. Böttger observed that when hydrogenized palladium black is exposed to air, it becomes very hot, and may detonate like gunpowder; L. Wöhler said that the hydrogenized palladium black is pyrophoric. W. Davies studied the rate of rise of temp. of the metal when hydrogen is burnt on the surface, and found that the combustion of hydrogen begins at 120°. F. E. Carter stated that palladium begins to acquire blue and red films as it oxidizes to the monoxide between 600° and 700°; this oxide is decomposed at about 900° into palladium and oxygen. According to T. Wilm, when palladium is heated in air in an open porcelain crucible with an ordinary burner, it rapidly darkens and turns a variety of colours, but on further heating it gradually assumes a dark, dirty, bluish-green hue, and then consists of a mixture of palladium and palladous oxide. When palladium sponge is heated in a stream of dry **oxygen** until its weight is constant, it is completely converted into palladous oxide. L. Wöhler observed in oxygen that under atm. press., palladous oxide is formed below 860°, and decomposed above that temp. The reaction $PdO \rightleftharpoons Pd+\frac{1}{2}O_2$ is reversible. The dissociation press. of different specimens above 750° are a little different. At 877°, the dis-

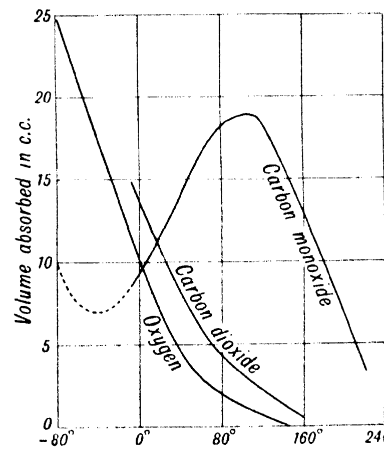

FIG. 10.—The Absorption of Gases by Palladium.

sociation press. attains the value 760 mm. The complete oxidation of palladium is difficult because of the sintering of the metal, and the slowness of the attack. The press. observed depends on the relative quantities of oxide and metal present and also on the time of heating. The greater the relative amount of metal the lower is the press. The results are best explained by supposing that palladium slowly dissolves in the oxide, forming a solid soln. the dissociation press. of which is lower than that of the pure oxide. The dissolution takes place very slowly, so that the pressure observed depends on the time of heating. W. Davies discussed the subject. G. Tammann and J. Schneider noted that the rate of growth of the film developed on palladium in air at 400° and 750° follows an exponential law. According to L. N. Vauquelin, when palladium is heated to its b.p. on charcoal in a jet of oxygen, or, according to E. D. Clarke, when it is heated in the oxyhydrogen flame, the metal burns with the emission of red sparks. L. Mond and co-workers found that palladium black at ordinary temp. absorbs oxygen vigorously from atm. air—and the heat developed is 1120 cals. per grm. of palladium. H. St. C. Deville found that palladium melted in an oxidizing atm. spits vigorously on solidification, thus showing that the solubility of oxygen in the molten metal is greater than it is in the solid. W. Ramsay observed that hydrogen unites with oxygen in the presence of palladium foil at 280°; and F. C. Phillips, that union occurs at 20° in the presence of palladized asbestos; and he placed the platinum metals Os, Pd, Pt, Ru, Ir, Rh, and Au in the order of their decreasing catalytic activities. The subject was studied by R. C. Smith. M. V. Tolyakoff, and H. Remy and co-workers gave Ir, Pd and Pt, when the other three metals were inactive. S. J. Roginsky and A. B. Schechter, and N. R. Dhar studied the reaction. D. L. Chapman and G. Gregory showed that the mechanism of the catalysis involves the alternate oxidation of the metal and the reduction of the oxide; that adsorbed hydrogen does not react appreciably with oxygen at the temp. of the laboratory; and that a film of adsorbed hydrogen can render the surface inoperative as a catalyst. According to W. Hartmann, and C. Paal and W. Hartmann, the rate of combination of the hydrogen and oxygen in the presence of colloidal palladium is greatest when the two gases are in the exact proportions required to form water. An excess of oxygen retards the reaction, so that colloidal palladium differs from colloidal platinum in that with the latter, the maximum speed is attained when the vol. ratio $H_2 : O_2 = 2 : 1$. It is assumed that this result is connected with the greater absorptive power of palladium for hydrogen. The subject was studied by G. Langer, L. Vallery, H. Gille, J. Gerum, K. A. Hofmann, D. L. Chapman and G. Gregory, and N. D. Zelinsky and P. P. Borissow. W. W. Hurst and E. K. Rideal observed the promotor action of palladium in the oxidation of hydrogen by a copper catalyst. K. A. Hofmann and O. Schneider found that in the oxidation of hydrogen in the presence of sodium chlorate soln. the catalytic activity of the metals decreased in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag. Dry or moist **ozone** has no action on palladium.

R. Böttger observed that when hydrogenized palladium is placed under **water**, there is first a violent evolution of gas; this ceases in 15 to 30 minutes, and it may then be kept for a month under the liquid without losing its catalytic activity. Water has no appreciable chemical action on palladium. W. Traube and W. Lange studied the decomposition of water by ferrous hydroxide or carbonate in the presence of palladium. G. Bredig and M. Fortner observed that the presence of palladium stimulates the decomposition of **hydrogen dioxide**; with $\frac{1}{60}N$-NaOH, $0{\cdot}1N$-H_2O_2 is as sensitive to a gram of colloidal palladium as 260×10^6 grms. of water; the presence of hydrogen favours the reaction, but the reaction is hindered by the presence of iodine, hydrogen sulphide, and mercuric chloride, and prevented by traces of hydrocyanic acid, or arsine. The reaction is favoured by the presence of sodium hydroxide, and the optimum conc. is about $\frac{1}{16}N$-NaOH; acids retard the reaction. The action was studied by G. Tammann, A. Coehn and K. Sperling, T. F. Macrae, J. Weiss, and G. R. Levi. R. Wright and R. C. Smith observed the

diminished activity with an increased temp. of preparation of palladium black, and A. de Gregorio y Rocasolano, on the temp. and age of colloidal palladium—with age, the activity of the soln. increases to a maximum and then decreases. C. Paal and C. Amberger placed the colloidal metals in the order of decreasing activity: Os, Pd, Pt, and Ir. R. C. Smith, and R. Wright and R. C. Smith compared the catalytic effect of amorphous and crystalline palladium—*vide* platinum; N. D. Zelinsky and P. P. Borissow, the effect of the hydrogenation of the palladium. E. Leidié and L. Quennessen observed a soluble palladite is formed when palladium is heated with **sodium dioxide.**

According to H. Moissan, **fluorine** at a dull red-heat transforms palladium into the difluoride; and O. Ruff observed that the attack begins at a red-heat, forming a yellowish-brown, crystalline crust presumably of the tetrafluoride. R. J. Kane, and E. H. Keiser and M. B. Breed found that dry **chlorine** attacks spongy palladium at dull redness to form palladous chloride; the metal is also readily attacked by chlorine-water. O. Ruff observed no action with the metal in contact with **chlorine trifluoride.** According to P. A. von Bonsdorff, and J. Nicklès, the metal is also attacked by a soln. of **bromine** in ether, and also by bromine water. J. J. Berzelius observed that palladium foil turns black when an alcoholic soln. of **iodine** is evaporated to dryness on the metal—platinum, similarly treated, remains bright. J. L. Lassaigne found that when palladium foil is heated in iodine vapour, it acquires a coloured film which afterwards turns brown—the application of heat or treatment with ammonia restores the brightness of the metal. When finely-divided palladium is heated with iodine in a glass tube, or treated with iodine-water, the union of the two elements is incomplete. W. Engelhardt observed no action between iodine and colloidal palladium. W. Engelhardt studied the action of palladium soln. on iodine. Chlorine and iodine unite with hydrogen in darkness in the presence of palladium or of hydrogenized palladium; according to T. Graham, chlorine water forms hydrochloric acid, and iodine-water, hydriodic acid. M. Berthelot observed no attack on **hydrogen chloride** at 550°. According to T. Wilm, N. W. Fischer, and W. J. Cock, compact palladium is slightly attacked by conc. **hydrochloric acid,** but the finely-divided metal is more readily attacked—the dissolution of the metal was found by C. Matignon, and A. M. Vasileff to be hastened in air; and it is also favoured by the presence of free chlorine. W. J. Cock observed that palladium black obtained by zinc precipitation easily dissolves in hot hydrochloric acid. H. E. Patten could not detect any action by hydrogen chloride in soln. of chloroform, carbon tetrachloride, ethyl chloride, benzene, silicon tetrachloride, stannic chloride, phosphorus trichloride, antimony trichloride, sulphur monochloride, or thionyl chloride. H. St. C. Deville observed that conc. **hydriodic acid** converts palladium into the diiodide. E. V. Zappi observed that a mixture of conc. hydrochloric acid and **chloric acid** is a useful solvent for palladium. According to T. Graham, hydrogen and palladium reduce **potassium chlorate** to chloride. G. Lemoine studied the catalytic action of palladium black on the reaction between **iodic acid** and oxalic acid.

J. J. Berzelius observed that when palladium is heated with **sulphur** chemical union occurs with incandescence. P. Anderson, and Y. Venkataramaiah and M. V. N. Swamy found that hydrogen which was passed over palladium black, or diffused through palladium, unites with sulphur at ordinary temp.—*vide supra.* A. Jedele observed that palladium sulphide is very sparingly soluble in the metal, and that the effect of sulphur on the yield point and fracture, in kgrms. per sq. mm., and the percentage elongation at room temp., and at 850°, are indicated in Table I. E. B. Maxted, and L. W. McKeehan found that the absorptive power of palladium black for hydrogen is considerably reduced by the presence of **hydrogen sulphide,** presumably owing to the formation of surface films of palladium sulphide. J. Uhl found that when palladium is heated in a current of **sulphur dioxide,** sulphur trioxide, and palladium sulphide are formed; and G. R. Levi and M. Faldini observed that the presence of palladium increased the activity of the platinum

TABLE I.—THE EFFECT OF SULPHUR ON THE TENACITY OF PALLADIUM.

S Per cent.	Room temperature			850°		
	Yield	Fracture	Elongation	Yield	Fracture	Elongation
0·32	13·2	29·5	17·2	—	—	—
0·15	12·5	28·8	17·6	—	—	—
0·04	12·5	26·5	17·8	—	—	—
0·02	11·5	25·5	20·4	—	—	—
0·003	8·9	20·6	26·5	5·6	8·11	18·8
0·001	9·2	19·4	24·2	5·1	6·6	16·8

catalyst in the oxidation of sulphur dioxide. J. H. Gladstone and A. Tribe found that with hydrogen and palladium sulphur dioxide is reduced to hydrogen sulphide. A. E. Patten observed no action with **sulphur monochloride** or with **thionyl chloride** at ordinary temp. N. W. Fischer, and W. H. Wollaston observed that boiling conc. **sulphuric acid** forms palladous sulphate and sulphur dioxide. W. J. Cock added that palladium black obtained by zinc precipitation easily dissolves in hot sulphuric acid. R. H. Adie observed that palladium with sulphuric acid begins to give off sulphur dioxide at 200°; no hydrogen sulphide is evolved, but some black palladium sulphide is formed. Unlike the case with platinum, J. J. Berzelius found that palladium, like rhodium, dissolves in fused **potassium hydrosulphate,** yielding the metal sulphate. M. G. Levi and co-workers studied the action of **potassium persulphate.** J. J. Berzelius, and F. Rössler found that when palladium is heated with **selenium** combination readily occurs with the evolution of heat.

A. Sieverts and E. Bergner observed that at 1400° to 1600°, palladium does not absorb **nitrogen.** A. Puodziukynas found that inactive, de-gassed palladium absorbs no nitrogen, but after activation by de-gassing in a high vacuum, 280 vols. of nitrogen were absorbed. J. Hagenacker studied the subject. H. Jellinek studied the action of nitrogen at high pressures on palladium. F. Hoppe-Seyler observed that nitrogen is oxidized by moist oxygen in the presence of palladium into ammonium nitrite. G. Gore said that the metal is insoluble in liquid **ammonia.** W. R. E. Hodgkinson and N. E. Bellairs found that the fused **ammonium sulphate or nitrate** dissolves palladium, forming an ammine. B. Ricca and F. Pirrone studied the reduction of hydrazoic acid by hydrogen in the presence of palladium. B. Ricca and F. Pirrone found palladium catalyses the reduction of **hydrazoic acid** by hydrogen. E. Hefti, L. Duparc and co-workers, E. Decarrière, and K. Kraut found that ammonia is oxidized by oxygen in the presence of palladium. E. Hefti, P. Sabatier and J. B. Senderens, and L. Duparc and co-workers, observed that hydrogenized palladium sponge in contact with **nitrous oxide** at 250°, and **nitric oxide** at 200°, forms water and ammonia. J. Bjerrum and L. Michaelis noted the catalytic effect in the oxidation of nitric oxide. W. Manchot and A. Waldmüller prepared **palladous dinitroxylchloride,** $PdCl_2.2NO_2$, by passing nitric oxide, saturated with the vapour of methyl alcohol, at 50°, over the anhydrous chloride. W. H. Wollaston said that palladium is dissolved by **nitric acid** at ordinary temp.; and that the metal dissolves more quickly in purified nitric acid than in that which contains nitrous acid—*confer* **3.** 21, 6, the action of nitric acid on copper. W. J. Cock observed that palladium dissolves slowly in nitric acid, but it readily passes into soln. when the palladium is alloyed with copper or silver; palladium black reduced by zinc dissolves easily in nitric acid. C. Fromme studied the electrochemical behaviour of nitric acid and palladium. J. H. Gladstone and A. Tribe found that palladium and hydrogen reduced **potassium nitrate** to potassium nitrite and ammonia. J. J. Berzelius observed that a mixture of fused potassium hydroxide and nitrate oxidizes the metal, but less readily than is the case with iridium, osmium, and rhodium. According to W. H. Wollaston, palladium is dissolved by **aqua**

regia at ordinary temp., and, according to P. A. von Bonsdorff, by a mixture of nitric and hydrobromic acids ; J. L. Lassaigne also found that the metal is attacked by a mixture of nitric and hydriodic acids. J. J. Berzelius observed that when a mixture of **phosphorus** and palladium is heated, a phosphide is formed. A. Jedele observed that palladium phosphide is very sparingly soluble in the metal, and that the effect of phosphorus on the yield point and fracture, in kgrms. per sq. mm., and the percentage elongation at room temp. and at 850°, are indicated in Table II.

TABLE II.—THE EFFECT OF PHOSPHORUS ON THE TENACITY OF PALLADIUM.

P Per cent.	Room temperatures			850°		
	Yield	Fracture	Elongation	Yield	Fracture	Elongation
0·265	13·2	28·2	19·5	—	—	—
0·098	11·2	26·2	26·6	—	—	—
0·021	12·7	25·0	26·8	—	—	—
0·006	12·2	23·9	23·4	3·1	4·1	15·0
0·000	12·7	22·4	23·1	4·8	5·3	9·2

E. Fink, and E. D. Campbell found that **phosphorus pentachloride** at 250° forms $PdCl_2.PCl_3$. H. E. Patten observed no action with **phosphorus trichloride** at ordinary temp. F. Loessner, P. Breteau, and A. Sieverts and E. Peters found that palladized copper facilitates the oxidation of **sodium hypophosphite :** $NaH_2PO_2+H_2O=H_2+NaH_2PO_3$, followed by $NaH_2PO_3+H_2O=NaH_2PO_4+H_2$; neither palladium foil nor wire stimulates the reaction, but colloidal palladium, palladium black, and electro-deposited palladium act as catalysts in the reaction. J. Böeseken and co-workers said that the amount oxidized in unit time is proportional to the weight of the catalyst ; the presence of hydrochloric acid, or sulphuric acid, retards the reaction, and sodium hydrocarbonate either is without action, or else it promotes the action very slightly. The catalyst slowly loses its activity in contact with the hypophosphite soln. R. Engel represented the catalytic reduction of copper hypophosphite by palladium : $Cu(H_2PO_2)_2+2H_2O=Cu+2H_3PO_3+H_2$. N. W. Fischer, and R. Chenevix said that the union of palladium and **arsenic** is attended by the evolution of heat. H. E. Patten observed that the metal is attacked by **arsenic trichloride** at ordinary temp. According to T. Graham, L. Thomassen, and A. C. Chapman, hydrogen and palladium reduce a soln. of **arsenic trioxide** to arsenic. H. E. Patten observed no action with **antimony tetrachloride** at ordinary temp. T. J. Poppema and F. M. Jäger studied the mol. hts. of the antimonides. A. T. Grigorieff, N. W. Fischer, and F. Rössler said that the union of palladium and **antimony** is attended by the evolution of light and heat. A. T. Grigorieff's study of the binary system showed that **palladium diantimonide,** $PdSb_2$, **palladium antimonide,** PdSb, and **palladium tritantimonide,** Pd_3Sb, melt respectively at 680°, 799°, and 1182° ; and R. Chenevix, C. T. Heycock and F. H. Neville, and F. Rössler observed that palladium alloys with **bismuth.** R. Engel found that palladium catalyzes the reduction of **antimony salts** by hypophosphorous acid, and similarly with **bismuth salts.**

J. R. Bréant observed that when palladium mixed with **carbon** is melted and cooled, the metal has become very brittle and friable. F. Wöhler, and H. B. Miller found that when heated in the sootless flame of a spirit-lamp, the palladium in the inner part of the flame, where the temp. does not rise above redness, acquires a black powder which when ignited forms grey, pulverulent palladium. Red-hot, spongy palladium laid on the wick of a spirit lamp, just extinguished, continues to glow and produce acetic acid as long as any alcohol remains in the lamp. At the same time, the palladium expands and " throws out cauliflower-like excrescences "

when this mass is removed from the wick it burns in air leaving a skeleton of palladium of the same form as the spongy palladium originally employed, but with ten times its bulk. H. Moissan observed that palladium does not combine with carbon, but the molten metal in the electric furnace dissolves carbon, which separates from the soln. in the form of graphite when the metal is cooled. H. Wölbling studied the adsorption of palladium by activated carbon. G. Harker showed that palladium deposited on carbon in an atm. of hydrogen, and exposed to X-rays forms $CH_3.NC$. E. Harbeck, and E. Harbeck and G. Lunge observed that palladium black absorbs 31 to 35 times its vol. of **carbon monoxide.** It is thought that a chemical compound is formed, but it has not been isolated, because, unlike mechanical absorption, the carbon monoxide is not driven from the product of hydrogen, and because when heated to 520°, the carbon monoxide is liberated suddenly. W. E. Garner gave 15 Cals. for the heat of adsorption of carbon monoxide and 9 Cals. for the heat of activation. J. Milbauer investigated the effect of palladium on the oxidation of carbon monoxide by sulphuric acid. The subject was studied by W. Davies. W. Manchot reported the three **palladous carbonyl chlorides :** $PdCl_2.CO$, $PdCl_2.2CO$, and $3PdCl_2.2CO$. P. V. McKinney, H. S. Taylor and R. M. Burns, H. S. Taylor and P. V. McKinney, K. Rauscher, J. Gerum, C. Paal and J. Gerum, studied the subject. P. V. McKinney's curve is shown in Fig. 10. L. Mond and co-workers observed the formation of a carbonyl. F. C. Phillips said that finely-divided palladium, or palladized asbestos in the presence of oxygen begins to oxidize carbon monoxide at 290°—W. Davies said 400°. W. Traube and W. Lange studied the reaction. K. A. Hofmann and O. Schneider observed that catalytic activity of the platinum metals in the oxidation of carbon monoxide in the presence of a soln. of sodium chlorate decreases in the order Os, Rh, Au, Pt, Ru, Pd, Ir, Ag. E. Baumann observed that carbon monoxide is oxidized to carbon dioxide in the presence of hydrogenized palladium and oxygen. M. Traube suggested that hydrogen dioxide acts as a carrier of oxygen for the oxidation, and F. Hoppe-Seyler, that the oxygen molecule is split into 2 atoms, one of which forms water with the hydrogen occluded by the palladium, and the other atom oxidizes the carbon monoxide, but the objection raised against this hypothesis is that ozone at 300° does not oxidize carbon monoxide, although it breaks down into free oxygen. W. W. Hurst and E. K. Rideal studied the promotor action of palladium in the adsorption and oxidation of carbon monoxide by copper ; and E. F. Armstrong and T. P. Hilditch the catalytic activity of palladium on the reaction : $CO+3H_2=H_2O+CH_4$. K. Jahn found that hydrogen and palladium will convert carbon monoxide into formaldehyde ; and F. Fischer and co-workers compared the activity of the platinum metals in reducing carbon monoxide to methane. A. de Hemptinne said that palladium which has previously occluded carbon monoxide loses the faculty of absorbing hydrogen at low temp. T. Graham observed that palladium is not permeable to **carbon dioxide.** P. V. McKinney's adsorption curve is shown in Fig. 10. H. S. Taylor and R. M. Burns studied the subject. J. Milbauer and J. Doskar examined the catalytic oxidation of **carbon disulphide** by sulphuric acid in the presence of palladium.

J. J. Coquillon observed that when the **hydrocarbons** are passed over heated palladium, they are decomposed into carbon and hydrogen, as T. Wilm, and F. Wöhler observed to be the case with ethylene. T. Wilm observed that if a current of coal-gas is passed over spongy palladium (reduced from the ammonium palladiochloride), heated over a Bunsen burner in a bulb-tube or small porcelain crucible, a large quantity of carbon is deposited on the inner walls of the crucible or tube, and after a time this collects over the edges of the crucible in cauliflower-like masses. This carbon, on combustion by a stronger heat, does not leave the least trace of palladium, nor does any deposition take place on the metal, which suffers no change of volume during the experiment. This action does not depend on the formation of a compound of carbon and palladium, but is due to the catalytic action of the metal, whereby the ethylene is decomposed with deposition of carbon. C. Paal

and C. Hohenegger studied the absorption of acetylene by colloidal palladium, and palladium black; and C. Zerbe and co-workers, the effect on the ignition of hydrocarbons; and E. K. Fritzman, R. Hocart, A. E. Mitchell and A. L. Marshall, G. Charlot, and C. Paal and A. Karl studied the activity of palladium as a catalytic agent. H. S. Taylor and R. M. Burns studied the adsorption of ethylene. The oxidation of hydrocarbons, etc., in the presence of palladized asbestos as catalytic agent, to carbon dioxide and water, proceeds at a much higher temp. than is the case with hydrogen; and the fractional combustion of such gases has been utilized by F. C. Phillips, W. Hempel, O. Brunck, and E. D. Campbell in the analysis of gases. Usually, the lower members of the same homologous series of hydrocarbons are more stable and offer a greater resistance to oxidation than do the higher members; the paraffin series is most difficult, and the olefine series is the most easy to oxidize; hydrogen oxidizes the most readily, then follow carbon monoxide, and acetylene. F. C. Phillips gave for the lowest temp. at which he could observe oxidation in the presence of air and palladized asbestos: hydrogen, 20°; **alcohol** vapour, 150°; **pentane,** 170°; **propylene,** 170°; **ethylene,** 180°; **isobutane,** 220°; **benzene,** 250°; carbon monoxide, 290°; **acetylene,** 339°; **propane,** 339°; **methane,** 404°; and **ethane,** 450°. In some cases, the products of the oxidation of the hydrocarbons are not carbon dioxide and water—thus, J. J. Coquillon found that no explosion occurred with a mixture of 2 vols. of oxygen and 1 vol. of methane when heated by a red-hot wire; but obtained benzyl aldehyde and benzoic acid from toluene; acetic acid from ethylene; and formic acid from methane; and F. Hoppe-Seyler converted benzene into phenol, and **toluene** into benzoic acid. P. Sabatier and J. B. Senderens observed that finely-divided palladium does not affect the thermal decomposition of ethylene. E. Tiede and W. Jenisch examined the influence of palladium on the pyrogenic decomposition of acetylene. H. E. Patten observed no action with benzene on palladium at ordinary temp.

H. E. Patten observed no action with palladium and **chloroform, carbon tetrachloride,** or **ethyl chloride** at ordinary temp. C. Paal and co-workers, and K. Yoshikawa studied the hydrogenation of **acetylene** with palladium as catalyst; C. Paal and W. Hartmann reduced ethylene to ethane; and M. Bourguel and V. Grédy, compounds with acetylene linkages—*e.g.* phenyl acetylene, and ethyl heptinene-carboxylate. Heated palladium in the presence of hydrogen, or hydrogenized palladium was found by H. Kolbe, T. Kariyone, O. Schmidt, and M. Saytzeff, to reduce hydrocarbons, and to convert **benzoyl chloride** into a mixture of benzyl aldehyde and benzyl alcohol; and **nitrobenzene** to aniline. C. Paal and C. Amberger compared the reducing power of the colloidal platinum metals on nitrobenzene in alcoholic soln. under similar conditions at 70°, and expressed the results in terms of the consumption of hydrogen in c.c. per hour by 1 c.c. of the metallic hydrosol:

Pd	Pt	Ir	Os
12,000 to 32,000	6,700 to 37,000	2,000 to 4,000	Small action

W. H. Carothers and R. Adams investigated the effect of platinum on the reduction of **benzaldehyde.** G. Lunge and J. Akunoff reduced benzene to tetrahydrobenzene by hydrogen and palladium. G. Scagliarini and G. B. Berti-Ceroni found oxalic acid is reduced by nitric acid in the presence of a palladium salt. N. D. Zelinksy and M. B. Turowa-Pollak studied the hydrogenation of benzene and the dehydrogenation of **hexamethylene** in the presence of palladium; E. Waser, the hydrogenation of sebacyl chloride; J. Böeseken and co-workers, cinnamic, muconic, aconitic, itaconic, citraconic, mesoconic, cyclopropane-1 : 1-dicarboxylic, ethylenetricarboxylic, and vinylglycollic acids; H. Wieland, the dehydrogenation of dextrose, lactic acid, gluconic acid, phenol, *m*-cresol, guaiacol, pyrogallol, aniline, alcohol, and acetaldehyde, but not tyrosine and uric acid; C. Kelber and A. Schwarz, phenylacetylene, tolane, and diphenyldiacetylene; P. Breteau, phenanthrene; C. Paal and W. Hartmann, phenylpropiolic acid; C. Paal and J. Gerum, benzo-

nitrite, mandelonitrile, benzaldoxime, fumaric acid, maleic acid, cinnamic acid, and methyl cinnamate; F. Plzak and B. Husek, and B. Rayman and O. Sube, the hydrolysis of sugar; N. D. Zelinsky, the reduction of iodides and bromides of cyclic alcohols; K. Kindler and W. Peschke, the methyl- and methoxy-cinnamic acids; A. A. Balandin, the dehydrogenation of cyclohexane; W. E. Keuntzel, and T. Sabalitschka and K. Zimmermann, the hydrogenation of fumaric acid; A. S. Grinsberg and A. P. Ivanoff, the hydrogenation of aliphatic compounds; E. Müller and K. Schwabe, the oxidation of ethyl alcohol. G. F. Hüttig and E. Weissberger studied the catalytic decomposition of **methyl alcohol.** K. Tanaka studied the reaction between methylene blue and alcohol in the presence of palladium; E. Müller and W. Loerpabel, and C. N. Hinshelwood and B. Topley, the catalytic action on **formic acid;** and R. L. Shriner and R. Adams, the reduction of **aldehydes.** J. H. Gladstone and A. Tribe, and M. Saytzeff reduced **nitromethane** to methylamine; and **nitrophenol** to amidophenol, but **acetic, benzoic, diglycolic, and lactic acids; ethyl oxalate; phenol** and **trinitrophenol,** were not reduced. S. J. Green studied the reduction of nitrocompounds. **Indigo-blue** was also reduced to indigo-white. C. Paal and A. Karl, O. Schmidt, and A. S. Grinsberg and A. P. Ivanoff found that magnesium, nickel, and cobalt favour the catalytic effect of palladium in the hydrogenation of unsaturated esters, but that aluminium, iron, copper, zinc, tin, silver, and lead act in the reverse way. C. Paal and J. Gerum, and C. Paal and C. Amberger studied the hydrogenation of nitrobenzene; T. Sabalitschka and W. Moses, the hydrogenation of maleic and fumaric acids, and sodium cinnamate; and C. H. D. Clark and B. Topley, the decomposition of formic acid. H. Wieland reported that palladium containing analytically significant quantities of hydrogen can remove hydrogen from **hydroquinone** to form quinone. L. J. Gillespie and J. H. Perry added that if this were true, all pressure-composition diagrams of the palladium-hydrogen system so far recorded have been made with unstable systems, for the press. are always measurable when appreciable quantities of hydrogen are present, and the press. of hydrogen at which it could be in equilibrium with hydroquinone and quinone in a reasonable mol. ration would be of the order of 10^{-24} atm. in accord with the e.m.f. measurements of E. Biilmann. L. J. Gillespie and T. H. Liu were unable to confirm the reaction, and concluded that there is no valid evidence showing that palladium containing an appreciable quantity of hydrogen can dehydrogenate hydroquinone. W. H. Hartung studied the hydrogenation of **oximinoketones** in the presence of palladium; and other hydrogenations of organic substances have been described by F. Mauthner. J. W. Kern and co-workers studied the reduction of olefines; and E. Raub, the action of onion, leek, and mustard juices. C. Paal and K. Roth observed that many unsaturated **vegetable oils**—*e.g.* butter, lard, linseed oil, olive oil, cod-liver oil, castor oil, croton oil, and cotton-seed oil—are completely reduced, hydrogenated, or "hardened" to form solid oils or fats when they are treated with hydrogen in the presence of colloidal palladium—sesamé oil and oleomargarine are incompletely reduced. Finely-divided nickel, or nickel oxide is employed industrially for the same purpose. W. Thomson and F. Lewis noted the destructive action of palladium on **rubber.** J. Ranedo studied the effect of palladium on the oxidation of organic matter by sulphuric acid.

C. Paal and C. Hohenegger, C. Paal, and A. Schwarz observed that palladium black, dry, or suspended in water or alcohol, absorbs 4000 vols.—and colloidal palladium about 5000 vols.—of acetylene per vol. of palladium. It is assumed that the acetylene is not absorbed as such, but forms polymerization or condensation products. The absorption continues several days—rapidly at first, and slowly later on. The absorption is favoured by raising the temp., or increasing the press. On exposure to air, part of the acetylene is evolved, and only a small amount is re-absorbed on exposure to acetylene. For the action of palladium sponge on alcohol, and for the oxidation and reduction of alcohol by oxygen or hydrogen, *vide supra.* A. Bringhenti studied the catalytic oxidation of soln. of sodium

methoxide, ethoxide, and *n*-propoxide by palladium. T. Graham found that palladium sponge, unlike platinum sponge, selectively adsorbs alcohol rather than water. When palladium sponge is left in contact with a mixture of alcohol and water in a sealed tube for 2 days, the supernatant liquor contains a smaller proportion of alcohol than before, and the palladium has adsorbed a greater proportion of alcohol than water. R. Böttger observed that when hydrogenized palladium is placed under alcohol, or **ether,** it behaves like it does under water —*vide supra*. N. D. Zelinsky found that a zinc-palladium couple reduces the iodides and bromides of the **cyclic alcohols.** T. Graham observed that hydrogenized palladium reduces **ferricyanides** to ferrocyanides. Palladium is said to be the only metal that will displace mercury from **mercuric cyanide.** H. E. Patten observed that no action on **silicon tetrachloride** occurs at ordinary temp.

E. Tiede and R. Piwonka studied the **alumina** palladium phosphors. According to F. E. Carter, palladium cannot be heated in a siliceous crucible without embrittlement by forming an alloy with **silicon.** L. I. Dana and P. D. Foote observed that silica may do the same thing—*vide infra*, platinum—**6**. 40, 14. C. Paal and W. Hartmann found that colloidal palladium converts **mercury** and **mercuric oxide** into colloidal soln., and at the same time loses its own catalytic activity possibly by forming a hydrosol of palladium amalgam; C. Paal and H. Steyer noted that colloidal hydrogenized palladium is dehydrogenized by mercury. T. Graham observed that palladium in the presence of hydrogen reduces **mercuric chloride** to mercurous chloride. H. E. Patten observed no reaction between **stannic chloride** and palladium at ordinary temp. C. A. Knorr observed that the rate at which hydrogen is removed from hydrogenized palladium by acidic soln. of **potassium dichromate** is proportional to the conc. of the oxidizing agent; it is determined by the rate of change at the interface and not by the rate at which hydrogen diffuses to the interface. Small quantities of hydrogen sulphide, arsine, carbon disulphide, iodine, and thiophen poison the surface and greatly retard the removal of hydrogen. G. Scagliarini and G. B. Berti-Ceroni studied the subject. T. Graham found that hydrogenized palladium reduces the dichromate **ferric salts** to ferrous salts. C. St. Pierre found that palladium reduces a soln. of **ferric chloride,** and a small proportion dissolves in the liquid. L. Kritschewsky, and V. Schwarzenbach and L. Kritschewsky found that hydrogenized palladium precipitates from their soln. silver, mercury (from the nitrates), gold, platinum, palladium, and copper in the metallic state; reduces acidified permanganates to manganous salts, ferric to ferrous salts, chromic acid to chromic oxide, potassium chlorate to hypochlorite, acetic acid to aldehyde and alcohol, and nitrobenzene to aniline. Salts of lead, bismuth, cadmium, arsenic, antimony, tungsten, molybdenum, zinc, cobalt, nickel, aluminium, cerium, uranium, rubidium, and cæsium, the alkalies and alkaline earths are not reduced. By employing the charged palladium in ample excess, and not leaving it too long in the soln., the reduction takes place quantitatively. H. Gille, and G. Brünjes studied the catalytic reduction of salts of zinc, cadmium, thallium, tin, lead, arsenic, bismuth, vanadium, columbium, molybdenum, tungsten, uranium, and iron salts by palladium. A. Krieger discussed the poisoning of the catalytic action of palladium on the dissolution of iron in acid by α-naphthoquinoline, and acridine. C. Fromme studied the electrochemical behaviour of palladium and chromic acid.

Some reactions of analytical interest.—Both **hydrogen sulphide** and **ammonium sulphide** will precipitate from acidic or neutral soln. of palladous chloride black palladous sulphide. N. W. Fischer[3] said that a yellow colour is produced by 1 part of palladium in 10,000 parts of liquid. The precipitate is insoluble in ammonium sulphide; but soluble in boiling hydrochloric acid, and in aqua regia. According to T. Rosenbladt, unlike lead, copper, and bismuth sulphides in the same analytical group, palladous sulphide is soluble in a soln. of potassium thiocarbonate, and unlike mercury sulphide, it is not precipitated from that soln. by carbon dioxide. Soln. of **potassium** or **sodium hydroxide**

precipitate a brown, basic salt soluble in a large excess of the precipitant; a soln. of **sodium carbonate** gives a brown precipitate of palladous hydroxide soluble in excess, but reprecipitated on boiling; and aq. **ammonia** gives a flesh-red precipitate of palladous dichlorodiammine, $[Pd(NH_3)_2Cl_2]$, soluble in an excess of aq. ammonia to form a colourless soln. from which hydrochloric acid precipitates the yellow, crystalline dichlorodiammine. Aq. ammonia does not give a corresponding precipitate with palladous nitrate, but forms a colourless soln. of the dinitratodiammine. A soln. of **potassium chloride,** with conc. soln., forms sparingly-soluble, reddish-brown crystals of potassium chloropalladite, insoluble in alcohol, soluble in water; **ammonium chloride** produces the corresponding ammonium salt. Palladic salt soln. behave in general like soln. of palladous salts, but **ammonium chloride** forms a sparingly-soluble ammonium chloropalladate, $(NH_4)_2PdCl_6$. The red precipitate is formed when a soln. of palladous chloride is oxidized by chlorine water, and treated with ammonium chloride. W. Singleton recommended as tests reactions with nitrosonaphthol, potassium or hydrogen iodide, mercuric cyanide, hexamethylenetetramine, and the formation of $PdFeCy_5(NO)$. A soln. of hydriodic acid, or of **potassium iodide,** gives a black precipitate of palladous iodide, even in dil. soln. of palladous chloride. The precipitate is insoluble in water, alcohol, ether, and hydriodic acid; but it is soluble in soln. of potassium iodide, and aq. ammonia. According to M. Baumann, the reaction slowly forms a few black flakes in a soln. with 1 part of palladium in 50,000 parts of liquid, but nothing with 1 in 500,000; and, according to J. L. Lassaigne, a brown coloration occurs with 1 in 400,000. A soln. of **potassium nitrite** precipitates, from not too dil. soln., yellow crystals which are soluble in water. Neutral or feebly acid soln. give with **mercuric cyanide** a yellowish-white, gelatinous precipitate of palladous cyanide sparingly soluble in hydrochloric acid, and readily soluble in potassium cyanide and aq. ammonia. No precipitate is produced by **potassium thiocyanate,** even after the addition of sulphurous acid. W. N. Ivanoff said that a precipitate is formed. In the absence of free hydrochloric acid, **stannous chloride** produces a brownish-black precipitate, and in the presence of free acid, a red soln. which becomes brown, and then green. The addition of water changes the colour to brownish-red. N. W. Fischer said that the limit of the reaction is 1 part of palladium in 100,000 of liquid. W. Schmidt, and F. Krauss and H. Deneke found that **α-nitroso-β-naphthol** produces a reddish-brown, voluminous precipitate unlike the case with other platinum metals. M. Wander and V. Thüringer, C. W. Davis, and F. Krauss and H. Deneke found that **α-dimethylglyoxime,** and J. Hanus and co-workers, that **benzoylmethylglyoxime,** gives a yellow precipitate which is soluble in ammonia and potassium cyanide soln., but sparingly soluble in water, 50 per cent. alcohol, and dil. acids. P. Claesson found that a yellow colour is produced in dil. soln. by a 1 per cent. aq. soln. of **ethyl-mercaptan,** and on acidifying the liquid with hydrochloric acid, and warming, a dark yellow, flocculent precipitate is immediately formed. F. Mylius and A. Mazzucchelli added that precipitates with iridium, ruthenium, and osmium salts require a prolonged heating. F. Feigl and co-workers found that a drop of silver soln., one drop of a 10 per cent. soln. of potassium cyanide, and one drop of an alcoholic soln. of ***p*-dimethylaminobenzylidene-rhodanine,** acidified with a drop of N-HNO_3, produces a violet coloration sensitive at a dilution of 1 : 500,000. N. A. Tananaeff and K. A. Dologoff said that a soln. of **benzidine** in acetic acid gives a blue or green colour in the presence of a drop of soln. containing not less than 0·00035 mgrm. V. G. Choplin said that no precipitate is produced by benzidine with palladous salts. S. C. Ogburn and A. H. Riesmeyer recommended **6-nitroquinoline** as a precipitant. H. Erdmann, O. Mekowka, H. Erdmann and O. Mekowka; and F. Krauss and H. Deneke found that **acetylene** precipitates from oxidic soln. a reddish-brown flocculent precipitate soluble in aq. ammonia, potassium cyanide, or sodium hydrosulphite. The reaction can be used for separating palladium from copper, platinum, and iridium. At 50°, **formic acid** or **sodium formate** precipitates palladium; **alcohol** does the same in the

presence of alkali hydroxide; and **hydrazine sulphate** in acidic or ammoniacal soln. precipitates palladium. The metal is also precipitated by **cuprous chloride** and **sulphurous acid**; and **mercurous nitrate** at first produces a brown precipitate and then slowly produces palladium, and, according to N. W. Fischer, the reaction is sensitive to 1 part of palladium in 100,000 parts of liquid; **ferrous sulphate** precipitates the metal—according to N. W. Fischer, the reaction is sensitive to 1 part of palladium in 1000 parts of liquid. F. Feigl and P. Krumholz observed that if 1 c.c. of a $0{\cdot}1N$- to $0{\cdot}5N$-acidic soln. be boiled with 5 drops of a 5 per cent. soln. of **phosphomolybdic acid,** and treated with a rapid current of carbon monoxide, a green or blue colour is developed by palladium but not by the other platinum metals. R. Nakaseko used **dimethylglyoxime.** W. N. Ivanoff found **sodium nitroprusside** forms a jelly with a soln. of a palladium salt; and **sodium thiocyanate,** a brown precipitate.

Some uses of palladium.—Palladium has not been utilized very much in the arts; an alloy with 62 per cent. of silver was once recommended for dental purposes; and alloys with gold have been proposed as substitutes for platinum for parts of astronomical instruments; as a coating for mirrors for searchlights owing to their resistance to atmospheric corrosion; in making dental alloys; and palladium leaf has also been employed in decorative arts as a white material comparable with gold leaf in screens and panels. Palladium salts have also been used in photographic work.[4]

Physiological action.—H. Coupin[5] observed that water containing 1 part of palladous chloride in 500,000 parts of water is toxic to the wheat plant. C. G. Gmelin found that palladium salts exert a corrosive action in the stomach, but the effects are not particularly toxic. An injection of palladous chloride coagulates the blood.

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§ 5. The Atomic Weight and Valency of Palladium

Palladium, like platinum, forms a monoxide, and a dichloride in which the element is *bivalent*, and bivalent platinum and palladium form isomorphous salts of the type: $K_2[PdCl_2(NO_2)_2]$. Palladium also, like platinum, is *quadrivalent* in forming a dioxide and a tetrachloride. L. Wöhler and F. Martin[1] described a hemitrioxide, Pd_2O_3, and complex salts with palladium trichloride, *e.g.* $2CsCl.PdCl_3$, in which palladium is *tervalent*. R. J. Kane's compounds of *univalent* palladium have not been established, although W. Manchot and H. Schmid obtained a salt of palladium in the univalent state. M. Gerber discussed some relations amongst the at. wts.; F. P. J. Dwyer and D. P. Mellor, and H. Reihlen and W. Hühn, the optical activity of the ammino-salts; and E. G. Cox and co-workers, the planar structure of the complex salts of bivalent palladium.

The equivalent weight of palladium is 53·5, and if this number be doubled for the at. wt., the results are in accord with (i) the sp. ht. rule; (ii) with the law of isomorphism applied to the isomorphism of the alkali chloropalladites and chloroplatinites, and to the alkali chloropalladates and chloroplatinates; and (iii) the position of palladium as the terminal member of the group of triads in the eighth group of the periodic table, and in the same vertical line as nickel and platinum in the eighth group in the periodic table.

In 1826, J. J. Berzelius calculated the at. wt. of palladium from the analysis of the monosulphide, and obtained a value of 113·91; a couple of years later, he analyzed potassium chloropalladite and obtained numbers ranging from 104·9 to 111·1. In 1847, Q. Icilius obtained 112·05 for the at. wt., a value based on the analysis of potassium chloropalladite. Nearly all these values are much too high, possibly because methods of purification of the salts known at the time were unsatisfactory. The results are only of historical interest. P. Gorceix discussed palladium acetylacetonate as a suitable salt for the determination of the at. wt. of palladium. Observations on the subject were made by K. Seubert.

The determination of the ratio $Pd(NH_3)_2Cl_2$ by E. H. Keiser furnished 106·49 and 106·51; E. H. Keiser and M. B. Breed, 106·46; H. F. Keller and E. F. Smith, 106·12 and 107·13; G. H. Bailey and T. Lamb, 105·70; A. Krell, 106·65; M. Woernle, 106·64 and 106·68; G. I. Kemmerer, 106·38; R. Amberg, 106·62, 106·65, and 107·31; and O. L. Shinn, 106·70. The ratio $2AgCl : Pd(NH_3)_2Cl_2$ furnished G. H. Bailey and T. Lamb, 106·61; and R. Amberg, 106·63 and 106·64. The ratio $Pd(NH_3)_2Br_2 : Pd$ furnished P. Haas, 106·68; H. Gebhardt, 106·67; and A. Gutbier and co-workers, 106·69. A. Joly and E. Leidié obtained from the ratio $2KCl : Pd$, 105·84, 105·95, and 106·25; from the ratio $K_2PdCl_4 : Pd$, 105·70 and 105·84; and from the ratio $K_2PdCl_4 : 2KCl$, 106·26 and 107·50. W. L. Hardin gave from the ratio $Pd(C_6H_5.NH_2Cl)_2 : Pd$, 107·00; from $Pd(C_6H_5.NH_2Br)_2 : Pd$, 107·01; and from $(NH_4)_2PdBr_4 : Pd$, 106·94; G. I. Kemmerer obtained from the ratio $Pd(NH_3)_2(CN)_2 : Pd$, 106·46. W. L. Hardin analyzed some complex salts; and O. L. Shinn considered that palladous dichlorodiammine has never been prepared free from ammonium chloropalladite, and, if so, the analyses of that salt are affected by the corresponding error. F. W. Clarke gave 106·7 for the best representative value; and the International Table for 1935 also gave 106·7.

The **atomic number** of palladium is 46. F. Allison and E. J. Murphy,[2] and W. Yeh obtained indications of three **isotopes**; A. J. Dempster, six isotopes—102, 104, 105, 106, 108, and 110—and F. W. Aston, none. J. H. Bartlett studied the subject.

According to F. W. Aston, elements other than hydrogen of odd atomic number do not have more than two stable isotopes, both of which have odd mass numbers excepting with elements of odd atomic number less than 8; and the isotope with the higher mass number is always heavier than the lighter by two mass units—*e.g.* copper with the atomic number 29 has the isotopes 63 and 65; and gallium of mass number 31 has the isotopes 69 and 71. In many cases, the element of even atomic number preceding the one with an odd atomic number in the periodic table has two missing isotopes of corresponding mass number. Thus, zinc of atomic number 30 has no isotopes 69 and 71 corresponding to the isotopes 69 and 71 of gallium of atomic number 31. H. J. Walke suggested that the missing isotopes are β-radioactive, and that the elements have been built up by a process of neutron capture, and β-radioactivity.

Several elements with odd atomic number are single isotope even when two isotopes are missing from the mass spectrum of the preceding element of even atomic number. Thus, rhodium has one isotope, ${}_{45}Rh^{103}$, although ruthenium has two isotopes, ${}_{44}Ru^{103}$ and ${}_{44}Ru^{105}$ missing from the mass spectrum of ruthenium. H. J. Walke then suggested that in these cases, the expected heavier isotope ${}_{45}Rh^{105}$ is also β-radioactive, so that the missing isotopes such as ${}_{44}Ru^{105}$ give rise to two successive β-transformations:

$$ {}_{44}Ru^{103} \rightarrow \beta\text{-rays} \rightarrow {}_{45}Rh^{103} $$
$$ {}_{44}Ru^{105} \rightarrow \beta\text{-rays} \rightarrow {}_{45}Rh^{105} \rightarrow \beta\text{-rays} \rightarrow {}_{46}Pd^{105} $$

The lightest palladium isotope is then evolved as the result of the emission of β-rays from the missing ${}_{45}Rh^{104}$. The isotopes of these three elements are then related in accord with

Ruthenium (44) . .	96, 98, 99, 100, 101, 102,	...,		104,	...
		$\downarrow\beta$			$\downarrow\beta$
Rhodium (45) . .		103			
			$\downarrow\beta$		$\downarrow\beta$
Palladium (46) . .			104,		105, 106

I. Kourtschatoff and co-workers bombarded ruthenium with slow neutrons, and concluded that both the above reactions occur, whilst E. Fermi and co-workers observed β-radioactivity corresponding to the absorption of slow neutrons by rhodium due to ${}_{45}Rh^{104}$. H. J. Walke also worked out similar isotopic relations for thorium, protoactinium, and uranium.

Neither E. Rutherford and J. Chadwick, nor H. Pettersson and G. Kirsch observed the **atomic disruption** of palladium when bombarded by α-rays; but G. Kirsch found that disintegration does occur. The **electronic structure,** according to N. Bohr, and E. C. Stoner, is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 4, 6) for the M-shell; (2, 2, 4, 4, 4) for the N-shell; and (2) for the O-shell. The subject was discussed by M. Kahanovicz, H. Perlitz, P. D. Foote, E. Fermi, P. Ray, A. F. Richter, W. Hulme-Rothery, S. Kato, P. G. Kruger and W. E. Shoupp, A. E. van Arkel and J. H. de Boer, H. Lessheim and R. Samuel, C. D. Niven, G. I. Pokrowsky, and H. J. Walke.

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§ 6. Intermetallic Compounds and Alloys of Palladium

G. Tammann [1] examined the **sodium-palladium alloys** and found that the reduction of the f.p. of palladium by the dissolution of 0·56, 1·54, 2·22, and 3·34 grms. of sodium in 100 grms. of palladium was, respectively, 0·07°, 0·26°, 0·31°, and 0·40°. P. G. Ehrhardt observed that the **lithium-palladium alloy** is harder than palladium alone.

N. W. Fischer prepared **copper-palladium alloys** and noted that combustion occurs without the evolution of light and heat. W. J. Cock observed that an alloy with 20 per cent. of palladium is white and ductile. C. H. Anderson prepared alloys with 40 per cent. of copper. L. Graf made single crystals of the alloy; R. Chenevix, that a 50 per cent. alloy is yellowish-grey, brittle, and has a sp. gr. of 10·392; and E. D. Clarke, that the 50 per cent. alloy, prepared in the oxyhydrogen flame, takes a high polish, and is easily filed. R. F. Mehl calculated the internal press. The alloys are malleable and ductile. G. Natta, and C. Matano studied the diffusion of palladium in copper. R. Ruer found that the f.p. curve falls regularly from the m.p. of palladium, 1541°, to 1084°, the m.p. of copper. The curve, Fig. 11, for alloys rich in copper is nearly horizontal. There is no evidence of chemical combination, and the two elements form a complete series of solid soln. There are disturbances due to supercooling. J. A. M. van Liempt, R. Taylor, and G. Borelius

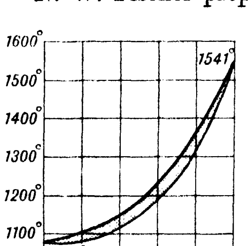

FIG. 11.—The Freezing-point Curve of Copper-Palladium Alloys.

and co-workers also investigated the equilibrium diagram. There is a complete series of solid soln. According to R. Ruer, when alloys with 30 to 70 per cent. of copper are etched with dil. aqua regia, slender acicular crystals appear. The proportion of these crystals is not appreciably altered by heating the alloy for 2 hrs. at 1500°, or at 1180°, and the proportion does not attain a maximum with an alloy of definite composition so that they do not indicate the formation of a definite compound. Alloys with up to 90 per cent. of palladium have the structure of copper; those with 10 per cent. of palladium are red, and those with over 20 per cent. are white. A. J. Bradley, and W. Nowacki discussed the X-radiograms. H. Röhl studied the elastic properties of the Cu_3Pd, and CuPd alloys; E. E. Halls, the hardness; R. F. Mehl, the internal pressures; and C. H. Johansson, the thermal expansion. S. Holgersson and E. Sedström found evidence of the formation of **palladium cupride**, PdCu. The cubic lattices of alloys with less than 39·7 and over 49·8 at. per cent. of palladium are face-centred, and those between these proportions are body-centred. The parameters $a \times 10^8$, and the sp. gr., are:

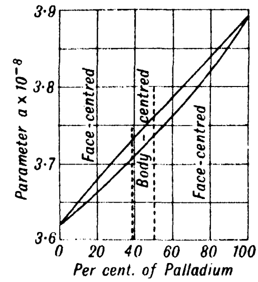

FIG. 12. — The Space-Lattice Constant of the Copper-Palladium Alloys.

Pd	0	19·4	36·4	45·5 at. per cent.
$a \times 10^8$	3·620	3·655	3·724	2·988
Sp. gr.	8·90	9·78	10·12	10·35
	Face-centred			Body-centred
Pd	51·9	54·4	70·2	100 at. per cent.
$a \times 10^8$	3·755	3·750	3·812	3·897
Sp. gr.	10·50	10·96	11·26	11·97
	Face-centred			

Observations were made by J. O. Linde, C. H. Johansson, and L. Nowack. V. Dehlinger studied the electronic structure. W. Biltz and F. Weibke discussed the volume relations of the constituents in forming the alloy. According to R. Ruer, the alloys are rather harder than the metals themselves, and the hardness is a maximum with alloys containing equal parts of copper by weight. E. Sedström's values for the thermal conductivity at 50°, expressed in watts per cm. per degree, and for the electrical resistance of a cm. cube in ohms$\times 10^6$ at 50°, are shown in Fig. 13; E. Grüneisen and H. Reddemann, H. J. Seemann, and A. Schulze made observations on the subject; and T. J. Poppema and F. M. Jäger studied the mol. hts. F. E. Carter found that the electrical resistance is less than with the copper-platinum alloys—alloys with 20 and 30 per cent. of copper have the respective resistances 270 and 250 ohms per million ft. The subject was studied by D. Stockdale, N. F. Mott, and B. Svensson. E. Sedstrom's values for the thermoelectric force, $E \times 10^{-6}$ volts per degree, of couples with the alloys against copper at 0° and at 100° are summarized in Fig. 14. In all cases, the singularities in the curves indicate the presence of a compound, and H. J. Seemann, N. F. Mott, B. Svensson, E. Vogt, and E. Vogt and H. Krüger studied the magnetic properties of the alloys. L. Nowack found that the range of chemical activity of the solid soln. of palladium-copper alloys is 0·22 mol. fraction of palladium for soln. of potassium or ammonium sulphide, and silver sulphate or nitrate; and 0·28 mol. fraction

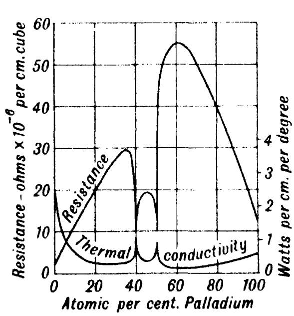

FIG. 13.—The Thermal Conductivity and Electrical Resistance of the Copper-Palladium Alloys.

for soln. of potassium or sodium hydroxide, alcoholic soln. of picric acid, palladium chloride, mercuric or mercurous nitrate, and mercuric chloride. Anodic evolution of oxygen occurs with alloys with 1·0 to 0·28 mol. of palladium. The voltage at which a stronger and continuous opposing current flows is the same for alloys with up to half a mol. of palladium. T. Graham observed that an alloy with one of palladium and six of copper is ductile and malleable, but does not occlude hydrogen; and similar remarks apply to the alloy with 50 per cent. of copper. The subject was discussed by L. Nowack, G. Tammann, and E. M. Wise and co-workers. E. F. Kingsbury used the alloy for electrical contacts; and C. A. Paillard, for non-magnetizable alloys for watches.

N. W. Fischer prepared **silver-palladium alloys,** and observed that the alloys are formed without the evolution of light or heat; G. Grube and D. Beischer studied

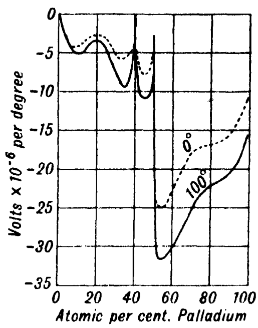

FIG. 14.—The Thermo-electric Force of the Copper-Palladium Alloys.

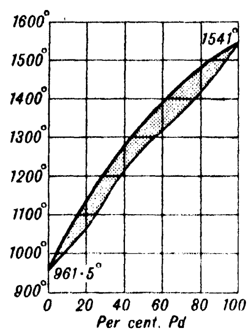

FIG. 15.—The Freezing-point Curves of Silver-Palladium Alloys.

the electrodeposition of the alloys; and R. Chenevix observed that an alloy with 50 per cent. of palladium is harder than silver, softer than iron, and has a sp. gr. of 11·29. G. Natta, and W. Jost studied the rate of diffusion of palladium in silver. R. Ruer observed that the f.p. of the alloys falls regularly from 1541°, the m.p. of palladium, to 961·5°, the m.p. of silver, and the curve is slightly concave to the concentration axis. The metals form a complete series of solid soln., without any indication of chemical combination. L. Tarshish, and E. Kordes studied the solid soln. L. W. McKeehan observed that the metals and the alloys have face-centred, cubic lattices with the parameter a, a linear function of the at. per cent. of either component. Thus, for cold-rolled and annealed alloys:

Ag .	100	90	75	60	50	40	25	10	0 at. per cent.
$a \times 10^8$.	4·080	4·056	4·037	4·001	3·982	3·969	3·945	3·921	3·900
Sp. gr. .	10·49	10·67	10·93	11·08	11·28	11·43	11·60	11·81	11·87

The values of a are rather larger for the cold-rolled alloys. The values for the sp. gr. are here included. F. Krüger and A. Sacklovsky noted that the expansion of the lattice by saturation with hydrogen is nearly the same for all the solid soln.; and the lattice saturated with hydrogen has a about 4·0 A. J. Weerts, and W. Stenzel and J. Weerts observed that the lattice parameter a of the face-centred cubic lattice is almost a linear function of the composition; the maximum contraction in a is 0·007 A. with a 1 : 1 alloy, Fig. 12. L. Nowack, and L. W. McKeehan studied the subject. L. Graf found that there is a transformation from α- to β-phases with alloys having 40 to 50 atomic per cent. of palladium. A. Osawa observed that the effect of hydrogenation is to expand the lattice constant of the silver-palladium

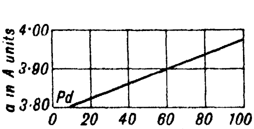

FIG. 16.—Lattice Parameters of the Ag-Pd Alloys.

alloys 3·6 to 3·87 per cent.; the maximum absorption of hydrogen occurs with alloys having 70 per cent. of palladium. The subject was studied by F. Krüger and G. Gehm. R. Nübel investigated the thermal energy of the alloys. R. Ruer observed that the hardness of the alloys lies between that of the components, and increases with the proportion of palladium. F. E. Carter found the Brinell's hardness, *H*, and Ericsen's ductility test in mm., to be:

Silver	10	20	30	40	60	80	90 per cent.
H Hard	130	294	282	248	130	114	95
H Annealed	74	248	190	122	88	59	53
Ductility	6·5	8·0	8·7	8·1	10·8	11·4	11·7

W. Geibel measured the tensile strength in kgrms. of wires 1 mm. diam., and the results are summarized in Fig. 17; there is a maximum with 50 per cent. of silver.

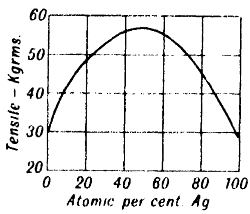

FIG. 17. — The Tensile Strength of Palladium-Silver Alloys.

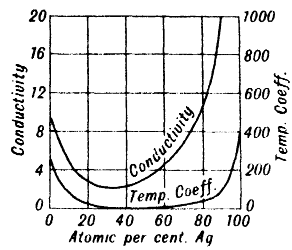

FIG. 18. — The Electrical Conductivity of Palladium-Silver Alloys.

J. A. M. van Liempt, and J. Dejmek studied the alloys. G. Wertheim made observations on the elasticity of the alloys. C. H. Johansson studied the thermal expansion; J. Schniedermann, the photoelectric effect and the thermoelectric effect with the alloys; and R. Glocker, the X-ray spectrum. R. F. Mehl calculated the internal press. of the alloys. G. Baiersdorf studied the spectrum analysis. The electrical conductivities at 0°, Fig. 18, have minima with about 40 per cent. of silver; and likewise also with the temp. coeff. of the conductivities between 0° and 160°. F. Krüger and A. Ehmer measured the photoelectric sensitiveness of the alloys. J. Dewar and J. A. Fleming, B. Svensson, J. MacGregor and C. G. Knott, A. Matthiesson, N. F. Mott, E. Vogt, and H. J. Seemann also studied the electrical conductivity of the alloys; and R. Sieverts and H. Hagen, the effect of hydrogen on the resistance. L. Nowack found that with alloys having 1·0 to 0·48 mol. proportion of palladium, the voltage at which a stronger and continuous opposing current flows is the same for alloys with up to 0·48 mol. palladium. G. Scatchard and W. J. Hamer studied the chemical potentials of solid and liquid soln. of Pd-Ag. W. Geibel's values for the thermoelectric force against platinum in millivolts are summarized in Fig. 19; and the thermoelectric forces of the different alloys in millivolts are summarized in Fig. 20. W. Broniewsky, J. Schneidermann, A. W. Smith, E. van Aubel, J. MacGregor and C. G. Knott also measured the thermoelectric properties of the alloys. R. Nübel found that the thermoelectric force of a wire of palladium-silver against a similar wire charged with hydrogen attains a maximum of 35×10^{-6} volt per degree with 40 per cent. of silver. The direction of the current with alloys containing up to 90 per cent. of silver is the same as it is with palladium wires—palladium negative. J. Wortmann, and E. van Aubel studied the Hall effect; and B. Svensson, E. Vogt, and

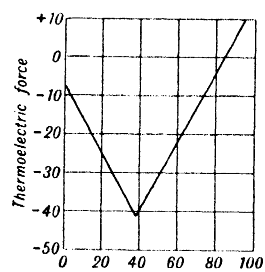

FIG. 19.—The Thermo-electric Force of Palladium-Silver Alloys.

N. F. Mott, the magnetic properties of the alloys. T. Graham observed that an alloy with 55·6 per cent. of copper absorbs 20 times its vol. of hydrogen at a dull red-heat; an alloy with 66 per cent. of palladium absorbs 411 times its vol. of hydrogen, and thereby expands 4·97 per cent. so that its sp. gr. is 11·45. A. Sieverts and co-workers found that for temp. between 138° and 820°, and at atm. press. downwards, the solubility of hydrogen is proportional to the sq. root of the press. Although hydrogen is virtually insoluble in silver, the addition of silver to palladium greatly increases the solubility until a maximum is reached for all temp. with 40 per cent. of silver; with more silver, the solubility rapidly diminishes as indicated in Fig. 21. At 138°, an alloy with 40 per cent. silver dissolves more than four times as much hydrogen as is the case with palladium, and the solubility becomes zero with 70 per cent. of silver. The relative increase of solubility in the case of an alloy with 40 per cent. of silver increases with falling temp. until 270°, but diminishes as the temp. falls further. If S_{Pd} denotes the

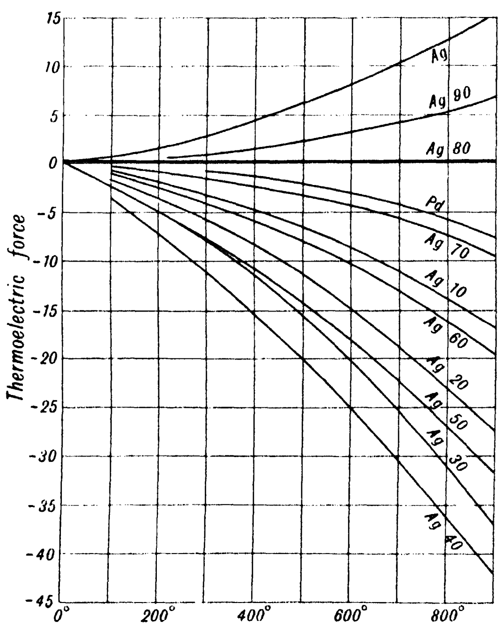

FIG. 20.—The Thermoelectric Force of the Palladium-Silver Alloys.

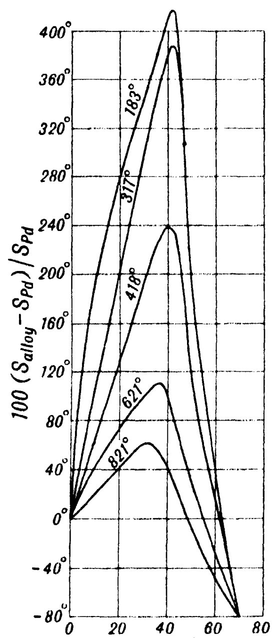

FIG. 21. — The Solubility of Hydrogen in the Palladium-Silver Alloys.

solubility of hydrogen in 100 grms. of palladium; and S_{alloy}, the solubility of hydrogen in 100 parts of alloy, $100(S_{alloy}-S_{Pd})/S_{Pd}$ denotes the percentage solubility of hydrogen in the alloy, Fig. 21. G. Rosenthal observed that the palladium-silver-hydrogen alloys have a face-centred cubic lattice with the constant varying with composition. The maximum solubility of hydrogen occurs with pure palladium. Observations were also made by G. Borelius, A. Coehn and H. Baumgarten, A. S. Grinsberg and A. P. Ivanoff, F. Krüger and A. Sacklovsky, L. Nowack, R. Nübel, A. Osawa, W. Rosenhain, O. Schmidt, G. Tammann, J. Spanner, and E. M. Wise and co-workers. G. Tammann studied the catalysis of electrolytic gas by palladium-silver alloys. E. M. Wise prepared **palladium-silver-copper alloys.**

N. W. Fischer prepared **gold-palladium alloys,** and found that the alloying occurs without the evolution of light or heat. R. Chenevix found that the alloy with 50 per cent. of gold is grey, as hard as bar-iron, less ductile than either com-

ponent, coarse-grained, and with a sp. gr. 11·079; W. J. Cock found an alloy with 80 per cent. of gold is white, hard, and ductile; and W. H. Wollaston, that an alloy with Pd : Au=1 : 6 by weight, is nearly white. K. Fischbeck, A. Jedele, and W. Jost studied the rate of diffusion of palladium in gold. F. E. Carter said that the high m.p., the non-oxidizability, and the chemical stability of the alloys has been applied in the production of laboratory ware with alloys having trade-names *palau*, *rhotanium*, and *palorium*. The early *white-gold alloys* used in jewellery were gold-palladium alloys, but they have been replaced by gold-nickel alloys which are harder and whiter. H. S. Washington used an 80 per cent. gold alloy for crucibles; and H. Limbourg used an alloy of 75 to 85 per cent. of gold, 10 to 15 per cent. of palladium, and 2·5 to 10 per cent. of platinum as a substitute for platinum. O. Feussner, and L. S. Rainer studied the gold-coloured alloys; and E. M. Wise and J. T. Eash, the palladium dental alloys. According to R. Ruer, the f.p. curve falls continuously from the m.p. of palladium, 1541°, to 1064°, the m.p. of gold, and it is concave to the axis of composition. The metals form a continuous series of solid soln., and there is no indication of chemical combination. The alloys with over 10 per cent. of palladium are white. There is no tendency for the alloys to segregate. J. A. M. van Liempt, and L. Tarshish studied the alloys. S. Holgersson and E. Sedström found that the lattice is a face-centred cube with the parameter $a\times10^{-8}$, and sp. gr.:

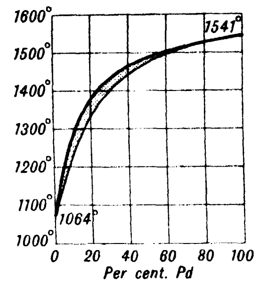

FIG. 22.—The Freezing-point Curve of Gold-Palladium Alloys.

Pd . . .	0	18·6	30·4	49·8	52·0	57·8	61·1	75·2	100·0 %
$a\times10^{-8}$ . .	4·080	4·030	4·001	3·975	3·965	3·959	3·950	3·925	3·897
Sp. gr. . .	19·28	18·30	17·59	16·08	15·99	15·50	15·29	14·18	11·97

The curve for the parameter, *a*, is smooth and convex to the composition axis. W. Stenzel and J. Weerts also found that the lattice parameter *a* is a linear function of the composition. Observations were made by W. C. Phebus and F. C. Blake, and H. Mundt. J. Weerts found the dimensions of the parameters of the face-centred cubic lattice of the alloys shown in Fig. 23. H. Röhl studied the elastic properties of these alloys. According to R. Ruer, the hardness of the alloys increases with increasing proportions of palladium up to 70 per cent., beyond which the hardness decreases. R. F. Mehl studied the internal press. F. E. Carter gave for Brinell's hardness, *H*, Ericsen's ductility test in mm., and the resistance, *R* ohms per million ft.:

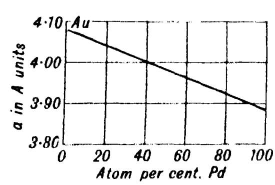

FIG. 23.—The Lattice Parameter of the Au–Pd Alloys.

Gold . .	10	20	30	40	60	80	90 per cent.
H Hard . .	124	135	180	192	190	165	120
H Annealed .	95	100	128	118	101	94	70
Ductility .	10·9	9·7	11·3	11·2	8·8	10·6	11·2
R . . .	99	113	145	161	165	109	67

C. H. Johansson studied the thermal expansion; and E. Grüneisen and H. Reddemann, the thermal conductivity. W. Geibel's results for the tensile strength, in kgrms., of wires 1 mm. in diameter are summarized in Fig. 24; his results for the electrical conductivity $\times10^4$ at 0°, the temp. coeff. of the conductivity between 0° and 160° are shown in Fig. 25; and for the thermoelectric force in millivolts against platinum at 1000°, in Fig. 26. J. O. Linde discussed the atomic resistance; A. Sieverts and H. Hagen, the effect of hydrogen on the electrical resistance; and W. Jost and R. Linke, the electrolysis of the solid alloy.

The effect of temp. on the thermoelectric force is summarized in Fig. 27. J. Wortmann, and E. van Aubel studied the Hall effect; J. Schniedermann, the thermoelectric and the photoelectric effect with the alloys; and N. F. Mott, the electrical conductivity, and the magnetic susceptibility. Some observations were made by L. Holborn and A. L. Day. A. D. van Riemsdyk observed that the alloys exhibit flashing during cupellation. B. Svensson, and E. Vogt discussed the magnetic properties of the gold-palladium alloys. According to T. Graham, an alloy with 75·21 per cent. of palladium has a sp. gr. 13·1, and it absorbs

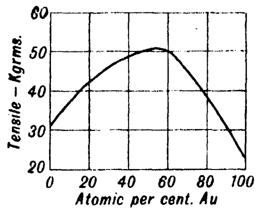

FIG. 24. — The Tensile Strength of the Gold-Palladium Alloys.

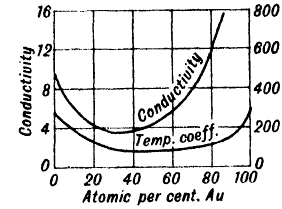

FIG. 25.—The Electrical Conductivity of the Gold-Palladium Alloys.

464 times its vol. of hydrogen when used as cathode in the electrolysis of acidulated water. It thereby expands 5·83 per cent. A. J. Berry measured the relation between the proportion of occluded hydrogen and of gold in the alloys. A. Sieverts and co-workers observed that between 138° and 820°, the solubilities for press. below 1 atm. are proportional to the sq. root of the press. The addition of gold to palladium first increases and then diminishes the hydrogen solubility up to a maximum. The maximum occurs at lower concentrations of gold, the higher the temp., Fig. 28, until, at 827°, any addition of gold lowers the solubility. The subject was studied by F. Krüger and E. Nähring, and E. Nähring; and G. Tammann examined the catalytic effect of the alloy on electrolytic gas. L. Quennessen studied the attack by caustic alkalies. F. A. Fahrenwald, H. S. Washington, P. Nicolardot and C. Chatelot, L. Quennessen, and L. J. Gurevich and E. Wichers discussed the use of alloys of palladium and gold as substitutes for platinum—*vide supra.* E. M. Wise and co-workers studied dental alloys containing gold and palladium. J. J. Berzelius discussed the native ternary alloy of **gold-palladium-silver alloy** called **porpizite**—*vide supra*—P. D. Merica, **palladium-gold-copper alloys**; L. Nowack, the **gold-palladium-zinc alloys**; and W. Fränkel and A. Stern, the **gold-palladium-nickel alloys.** E. D. Clarke obtained a **barium-palladium alloy** before the oxyhydrogen flame. The silver-white alloy acquires a film of oxide after 24 hrs.' exposure. W. R. E. Hodgkinson and co-workers prepared a **magnesium-palladium alloy** by passing the vapour of magnesium over heated palladium. N. W. Fischer observed that the formation of **zinc-palladium alloys** is attended by the evolution of light and heat. The alloy is brittle. W. R. E. Hodgkinson and co-workers prepared the zinc alloy by passing the vapour of zinc over heated palladium. A. Westgren, W. Ekman, A. J. Bradley, and W. E. Schmid discussed the X-radiograms. H. St. C. Deville and H. Debray observed that dil. and cold-hydrochloric acid dissolves all the zinc and leaves the palladium; and N. W. Fischer observed that some palladium passes into soln. L. Nowack studied the age hardening of the **palladium-gold-zinc alloys.** W. R. E. Hodgkinson and co-workers prepared a **cadmium-palladium alloy** by passing the vapour of cadmium over heated palladium. C. T. Heycock and

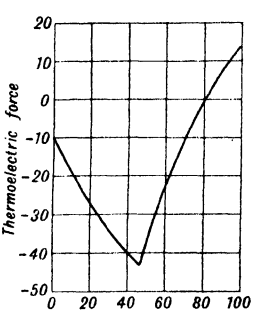

FIG. 26.—The Thermo-electric Force of Gold-Palladium Alloys.

F. H. Neville studied the lowering of the f.p. of cadmium by palladium. The occurrence of **palladium amalgam,** as the mineral **poterite,** was discussed by L. J. Spencer—*vide supra*, the occurrence of palladium. W. H. Wollaston obtained mercury-palladium alloys by agitating the aq. soln. of a palladium salt with an excess of mercury; J. J. Berzelius added that if the palladium salt be in excess, the grey powder which is produced contains Pd_2Hg, and does not give up its mercury at a red-heat, but only when heated to whiteness. The amalgam can be obtained by triturating the freshly-prepared, and finely-divided palladium with mercury. Union occurs with the evolution of heat, and sometimes with an explosion. The palladium becomes less active after it has been exposed to air. P. Casamajor obtained the amalgam by placing palladium in contact with mercury, and a zinc rod, and covering them with acidulated water. G. Langer prepared

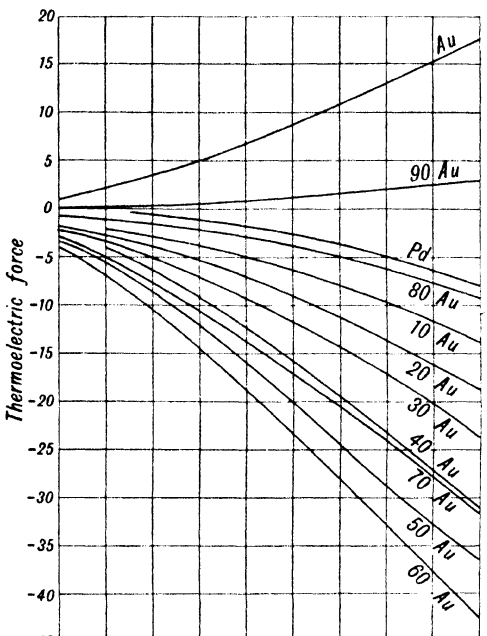

FIG. 27.—The Thermoelectric Force of the Gold-Palladium Alloys.

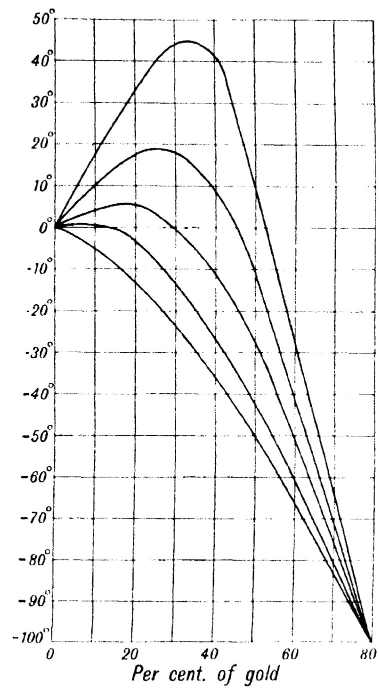

FIG. 28.—The Solubility of Hydrogen in Gold-Palladium Alloys.

palladium amalgam hydrosol with sodium probalbinate and lysalbinate as protective colloids. The amalgam has been used as a filling for teeth. H. Debray, and C. Margot prepared some **aluminium-palladium alloys.**

H. St. C. Deville and H. Debray prepared a **tin-palladium alloy**; and C. T. Heycock and F. H. Neville studied the action of palladium on the f.p. of tin. N. W. Fischer found that the formation of **lead-palladium alloys** is attended by the evolution of light and heat; and R. Chenevix described the alloy as grey, hard, brittle, fine-grained, and of sp. gr. 12·0. A. Bauer also obtained the alloy, and removed the excess of lead by acting on it with acetic and carbonic acids. The alloy remaining after the attack of acetic acid had a composition Pd_3Pb, and the steel-grey, crystalline product has a sp. gr. 11·225. C. T. Heycock and F. H. Neville studied the effect of palladium on the f.p. of lead. R. Ruer found that the f.p. curve, Fig. 29, has a maximum at 454° and 20 per cent. of lead, corresponding with **palladium diplumbide,** $PdPb_2$; and another maximum at 1219° and 61 per

cent. of lead corresponding with the **palladium tritaplumbide,** Pd_3Pb, of A. Bauer. There are eutectics at 265° and 5 per cent. palladium, and at 1197° and 66 per cent. of palladium. There is a break at 495° corresponding with **palladium plumbide,** PdPb; one at 830° corresponding with **palladium hemiplumbide,** Pd_2Pb, both of which decompose below their m.p.; the break at 590° is not so definite and it corresponds with 37·5 to 40·7 per cent. of lead. Solid soln. are formed with 60 to 66 per cent., and 77 to 100 per cent. of palladium. Alloys with 20 to 90 per cent. of palladium are harder than their components, and the hardness is a maximum with 65 per cent. of palladium. Alloys with 17·5 to 60 per cent. of palladium are very brittle, and beyond 60 per cent. of palladium, the alloys become tougher. The subject was studied by G. Tammann.

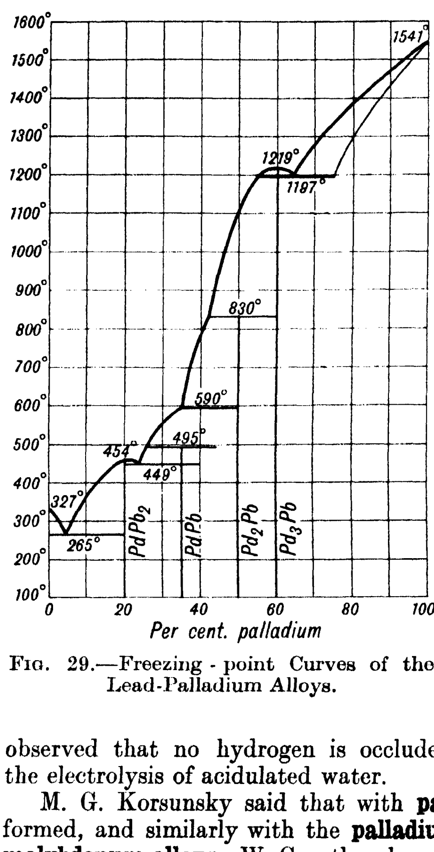

FIG. 29.—Freezing-point Curves of the Lead-Palladium Alloys.

N. A. Puschin and N. P. Pashsky measured the potentials of the alloys in the cell Pb : N-$Pb(NO_3)_2$: Pd-alloy. All the alloys with less than 33 at. per cent. of palladium have a potential like that of lead, but with over 33 at. per cent. of palladium, the potential at first is 350 to 400 millivolts, and then rises to 605 to 640 millivolts. The results are said to confirm the existence of palladium diplumbide. F. W. Constant measured the magnetic constants of the binary alloys and found that with 90 and 95 per cent. of palladium, the Curie points were, respectively, 235° and 82°, and the maximum intensity of magnetization obtainable at the temp. of liquid air, —194°, 223, and 193. A. Bauer observed that no hydrogen is occluded when Pd_3Pb is made the cathode in the electrolysis of acidulated water.

M. G. Korsunsky said that with **palladium-tantalum alloys,** solid soln. are formed, and similarly with the **palladium-chromium alloys,** and the **palladium-molybdenum alloys**—W. Guertler also prepared this alloy. E. F. Kingsbury used a **palladium-tungsten alloy** for electrical contacts. M. G. Korsunsky said that solid soln. are formed. A. T. Grigorieff found that the **palladium-manganese alloys** form a continuous series of solid soln. with a minimum m.p. between 39·3 and 45·0 per cent. of palladium. There is evidence of the formation of **palladium manganide,** PdMn. G. Grube studied the magnetic properties of these alloys.

N. Agéeff and M. Zamotorin measured the rate of diffusion of palladium in steel. J. Stodart and M. Faraday obtained **iron-palladium alloys,** and one with 1 part of palladium in 100 of steel had a good cutting edge. R. A. Hadfield studied these alloys; and J. R. Bréant prepared what he called palladium steel. A. T. Grigorieff observed no evidence of the formation of a compound on the cooling curves of the alloys. The solid phase consists of an unbroken series of solid soln. with a minimum on the f.p. curve, Fig. 30, at 1290° with 50 per cent. of palladium. Solid soln. with 75 atm. per cent. of palladium exhibit recalescence on cooling, indicating the existence of a **palladium tritaferride,** Pd_3Fe, with a transformation point at about 810°, and this hypothesis is in harmony with the hardness (Fig. 31), conductivity, and temp. coeff. of the conductivity (Fig. 32) curves. F. Wever studied the effect of palladium on the transition points of iron.

M. G. Korsunsky said that solid soln. are formed; and W. R. E. Hodgkinson and co-workers observed no evidence of the formation of any compound. H. Remy and H. Gonnington studied the catalytic effect on the hydrogen-oxygen reaction.

F. W. Constant studied the magnetic properties of **cobalt-palladium alloys.**

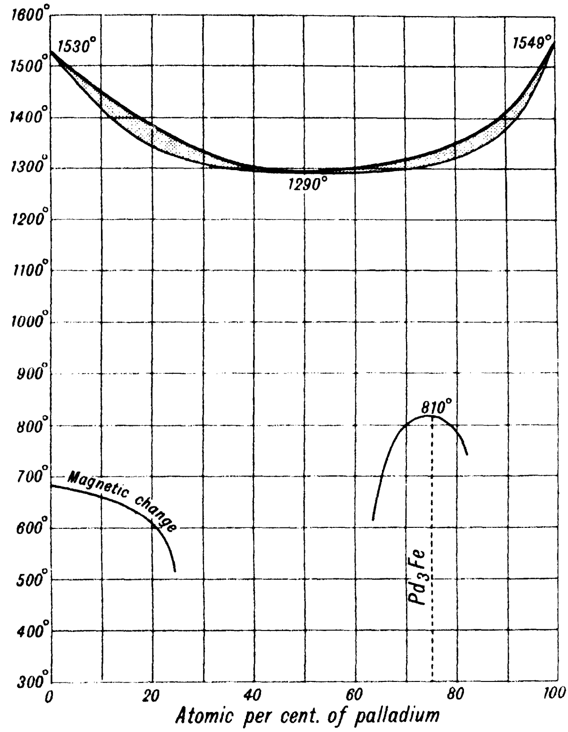

FIG. 30.—Freezing-point Curves of the Fe–Pd System.

M. G. Korsunsky said that solid soln. are formed. G. Grube and co-workers studied the resistance, and the magnetic properties of the alloys; and H. Remy and H. Gonnington the catalytic effect on the hydrogen-oxygen reaction.

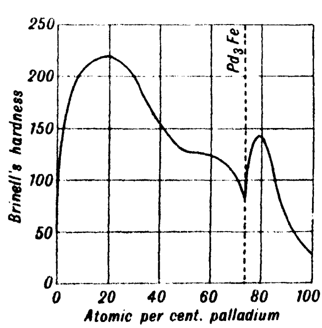

FIG. 31.—The Hardness of the Fe–Pd Alloys.

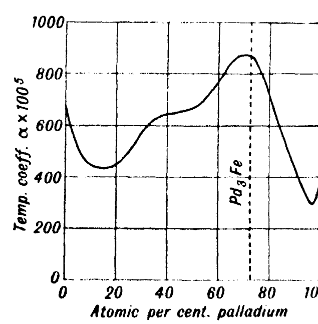

FIG. 32.—The Temperature Coefficient of the Electrical Resistance (25° to 100°).

E. D. Clarke prepared a **nickel-palladium alloy** before the oxyhydrogen flame. W. Nowacki discussed the *white gold alloys*. M. G. Korsunsky said that solid soln. are formed. F. Heinrich measured the f.p. curves, and the results are summarized in Fig. 33. There is a flat minimum at 1208°, with between 50 and 70 per cent. of

palladium. W. Fraenkel and A. Stern said that the minimum is near 60 per cent. of palladium. J. A. M. van Liempt discussed the alloys. A. T. Grigorieff also said that the system forms an unbroken series of solid soln. with the liquidus curve :

Palladium .	0	10·97	21·28	32·13	41·47	51·08 at. per cent.
Freezing at .	1480°	1473°	1468°	1476°	1508°	1539°

The curves for the magnetic transformation fall with increasing proportions of palladium, slowly at first, and rapidly beyond 40 per cent. of palladium, and at about 80 per cent. of palladium, the temp. of the magnetic change are the same on the heating and cooling curves. F. E. Carter found that alloys with 10 and 20 per cent. of nickel had Brinell's hardness for the annealed metal, respectively, 163 and 198, and electrical resistances of 145 and 138 ohms per million ft. A. T. Grigorieff observed a maximum hardness with 60 at. per cent. of palladium, and that the temp. coeff. of the conductivity curve has maxima at 20·3 and 80·8 at. per cent. of palladium. E. Sedström studied the resistance and the thermoelectric properties ; R. Forrer, and L. Néel, the magnetic properties of the alloys ; and H. Remy and H. Gonnington, the catalytic effect on the hydrogen-oxygen

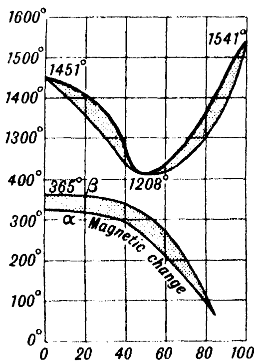

FIG. 33.—The Freezing Points of the Nickel-Palladium Alloys.

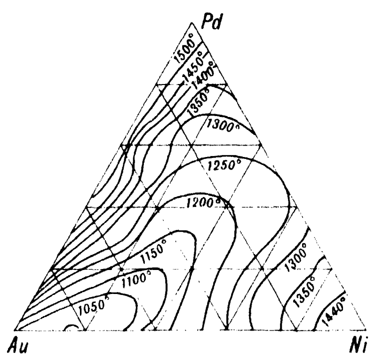

FIG. 34.—Freezing-point Curves in the System : Gold-Nickel-Palladium.

reaction. W. Fraenkel and A. Stern's results for the f.p. of the **gold-nickel-palladium alloys** are summarized in Fig. 34.

F. E. Carter found that **ruthenium-palladium alloys** form a series of solid soln., and that alloys with over 10 per cent. of ruthenium are too hard to work, and that Brinell's hardnesses for 5, and 7·5 per cent. alloys are for the hard metal 152 and 230, respectively, and for the annealed metal, 92 and 120. H. Remy and co-workers found the activity of palladium as a catalyst in the reaction between hydrogen and oxygen is augmented by alloying the metal with ruthenium. The **rhodium-palladium alloys** also form a series of solid soln. Alloys with 5, 10, and 15 per cent. of rhodium have Brinell's hardnesses, respectively, 134, 147, and 195 for the hard metal, and 72, 79, and 104 for the annealed metal ; whilst alloys with 5 and 10 per cent. of rhodium have electrical resistances, respectively, 126 and 155 ohms per million ft. The 50 : 50 alloys are friable and unworkable. G. Tammann and H. J. Rocha found that the rhodium-palladium alloys have a smooth hardness curve with a maximum at 50 to 60 at. per cent. of rhodium. The maximum solubility of hydrogen occurs with the alloy having 10 at. per cent. of rhodium. The reaction with an alcoholic soln. of iodine reaches a limit with 75 at. per cent. of rhodium. H. Klausmann and H. R. Kiepe, and B. Bart also prepared the alloys. E. M. Wise and J. T. Eash studied the hardness of the alloy with 4 per cent. of ruthenium and 1 per cent. of rhodium ; H. Remy and H. Gonnington, the catalytic effect on the hydrogen-oxygen reaction.

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§ 7. The Palladium Oxides

J. J. Berzelius [1] thought that the tarnish formed on palladium heated in air is due to the formation of **palladium hemioxide,** or **palladium suboxide,** Pd_2O; and T. Wilm added that the oxidation of palladium when heated in air produces the suboxide, but he later showed that the oxidation of the metal under these conditions is incomplete, and that the first product of the complete oxidation is palladium monoxide. G. Neumann reported that the suboxide is produced when the metal is heated at 450° in a current of oxygen. R. J. Kane said that the suboxide is produced as a black powder when palladium monoxide is heated to redness until oxygen is no longer evolved; at a higher temp., palladium and oxygen are formed. He said that palladium suboxide is decomposed by acids into the monoxide and metal. L. Wöhler, and L. Wöhler and J. König measured the dissociation press. of the monoxide, and found the curve continues with no sign of the formation of a suboxide. R. Schneider also reported **palladium pentitahexoxide,** Pd_5O_6, to be formed when potassium palladium sulphide is fused with sodium hydroxide and potassium nitrate. L. Wöhler and J. König, however, showed that it is probably palladium monoxide contaminated with some dioxide. This is confirmed by the X-radiograms of the alleged suboxide obtained by G. R. Levi and C. Fontana. The results showed that the lines corresponded only with those of palladium and of palladium monoxide. Each atom of palladium is surrounded by four co-planar atoms of oxygen at the corners of a square, whilst each atom of oxygen is surrounded by four atoms of palladium at the apices of a tetrahedron. L. Pauling and M. L. Huggins discussed the subject. W. Manchot and H. Schmid

found that dil. aq. soln. of potassium palladocyanide are reduced vigorously by sodium amalgam to univalent palladium, and that the soln. has more vigorous reducing qualities than the corresponding platinum soln. When shaken with air it yields hydrogen peroxide. When preserved at the ordinary temperature the initially colourless soln. becomes pale yellow and hydrogen is noticeably evolved. The colour gradually deepens, and finally black particles of metal separate which slowly increase in number. If the soln. is boiled, the metal is deposited copiously and hydrogen vigorously evolved. If the alkaline soln. is boiled before or after addition of acetic acid, hydrochloric acid, or potassium cyanide, hydrogen free from carbon monoxide is evolved in amount varying from 0·22 to 0·72 equivalent. A portion of the liberated hydrogen is utilized in other ways, since methylamine is present in the acetic acid soln. Titration with potassium ferricyanide or iodine requires amounts of reagent less than 1 equivalent, thus corresponding sharply with the transformation of univalent into bivalent palladium.

J. J. Berzelius prepared **palladium monoxide,** or **palladous oxide,** PdO, by strongly heating palladium amalgam; by treating soln. of palladous salts with alkali lye; and by fusing palladium with alkali hydroxide. N. W. Fischer, and J. J. Berzelius obtained it by heating palladous nitrate to dull redness, until the nitrogen oxides are all expelled; W. Zachariasen described the preparation of the monoxide by heating the dichloride with nitre at 600°. A sample of the monoxide obtained by heating palladium in oxygen at 830° for an hour followed by slow cooling, contained some metallic palladium; and R. L. Shriner and R. Adams obtained the monoxide by heating palladous chloride with sodium nitrate at 600°. L. Wöhler and J. König said that the easiest mode of preparing the oxide is by hydrolyzing a faintly acidic soln. of the nitrate by boiling it with water. T. Wilm heated spongy palladium to dull redness in a current of oxygen. It is difficult directly to oxidize the metal completely because some sintering of the oxide is liable to occur, and subsequent oxidation is then slow. L. Wöhler obtained the best results by heating spongy palladium in oxygen at a temp. slowly rising from 700° to 840°. L. Wöhler showed that the reaction $Pd+\frac{1}{2}O_2 \rightleftharpoons PdO$ is reversible, and obtained for the dissociation press., and the equilibrium constant, K:

	685°	720°	770°	789°	810°	830°	858°	877°
p . .	10	26	94	148	220	331	590	771 mm.
$K \times 10^3$	0·409	0·648	1·203	1·496	1·806	2·195	2·894	3·281

the dissociation press. is 760 mm. at 877°. Analogous observations were made by R. Schenck and F. Kruzen. Higher values were obtained for the oxide prepared at a high temp. R. Schenk and F. Kurzen studied the subject. G. R. Levi and C. Fontana found that the X-radiograms of the monoxide correspond with a face-centred tetragon with $a=4·23$ A., $c=5·20$ A., and $a:c=1:1·23$. The sp. gr. is 8·73, when the observed value is 8·70 at 25°/4°. G. Lunde gave $a=3·029$ A., and $c=5·314$ A. W. Zachariasen found that the tetragonal cell has $a=3·029$ A., $c=5·31$ A., and $a:c=1·754$, and sp. gr. 8·31. G. Lunde studied the subject.

L. Wöhler and W. Müller gave for the observed dissociation press. 10 mm. at 680°; 41 mm. at 740°; 129 mm. at 780°; and 590 mm. at 860°. L. Wöhler and N. Jochum gave for the mol. ht., $C=7·184+0·014200\theta$. According to L. Wöhler—*vide supra*—the calculated values for the heats of formation are —23·6 Cals. between 711° and 819°; —23·4 Cals. between 711° and 866°; and —21·5 Cals. between 781° and 866°. The best representative value is 23·5 Cals. per atom of oxygen. L. Wöhler and N. Jochum gave 20·40 Cals. The results agree better with the assumption that the reaction is $PdO \rightleftharpoons Pd+O$ rather than $2PdO \rightleftharpoons 2Pd+O_2$. J. Thomsen gave $(Pd,O,H_2O)=22·7$ Cals., and J. A. Joannis, $(Pd,O)=20$ Cals. J. A. Joannis gave for the heats of neutralization of precipitated PdO with dil. acids: 2HCl, 10·8 Cals.; 2HBr, 14·8 Cals.; 2HI, 35·8 Cals; and 2HCy, 44·8 Cals. W. Zobel studied the radiation of oxidized palladium; and L. P. Davies, the X-ray emission. M. le Blanc and H. Sachse said that the conductivity of the oxide is small.

H. S. Taylor and P. V. McKinney found that palladium oxide is reduced by carbon monoxide at temp. below 100°; and P. V. McKinney and co-workers observed some reduction at 23°; but if adsorbed oxygen is removed, reduction does not occur below 76°; below 156°, reduction does not proceed to completion, but decreases in rate with time. The presence of carbon dioxide in the monoxide inhibits the reduction at 100°, and retards the completion of the reaction at 156°. The retardation is attributed to the strong adsorption of carbon dioxide on the oxide. Small proportions of oxygen accelerate the reduction which is then completed at 76°. Palladium reduced from the oxide is only slightly catalytic towards the reduction of carbon monoxide. The subject was studied by A. R. Ubbelohde. R. Schenck and F. Kurzen studied the reaction of the oxide with silica, without obtaining a definite silicate, and with alumina, which furnishes the **palladium aluminates,** $PdO.Al_2O_3$; $2PdO.Al_2O_3$; and $PdO.8Al_2O_3$.

The hydrated oxide prepared by the wet processes contains rather more water than corresponds with **palladous hydroxide,** $Pd(OH)_2$. The precipitated hydroxide separates with varying amounts of combined water, and the colour varies in a corresponding manner from yellowish-brown to black. Dried over sulphuric acid, it furnishes black, shining grains; when heated on a water-bath, it is brownish-black, the residual water approximates about two-thirds of a mol., but the last traces of the water were found by L. Wöhler and J. König to be not all expelled at 500° to 600°. The anhydrous oxide is obtained only by heating the hydrate at 800° to 840° in oxygen. Above this temp., the anhydrous, green monoxide decomposes. When precipitated in the cold, the hydrated monoxide is soluble in dil. acids, and in an excess of alkali lye; but when precipitated hot, and boiled in the mother-liquor, it is no longer completely soluble, even in boiling, conc. alkali lye. When dried at 100°, it is insoluble in acetic acid, and nearly insoluble in sulphuric and nitric acids. The anhydrous oxide is very sparingly soluble in hydrochloric acid, and in aqua regia. The oxide is reduced in the cold by hydrogen, evolving so much heat that the mass becomes incandescent. It turns diphenylamine blue; and it reduces hydrogen dioxide with difficulty. A. Mailfert said that ozone converts palladium monoxide into dioxide, and in the presence of potassium hydroxide, potassium palladate is formed. F. Bullnheimer said that palladium oxide is reduced to metal by glycerol. F. Müller and A. Riefkohl studied the solubility of palladous oxide in N-$NaNO_3$.

According to H. Müller, and H. D. K. Drew and co-workers, when palladous dichlorodiammine is treated with moist silver oxide, or when the sulphatodiammine is treated with the theoretical proportion of barium hydroxide, and the filtered soln. is evaporated in vacuo, or in air free from carbon dioxide, then **palladous dihydroxydiammine,** $[Pd(NH_3)_2(OH)_2]$, is formed, in yellow microscopic octahedra. The dry dihydroxydiammine does not decompose at 105°. The aq. soln. is strongly alkaline and rapidly absorbs carbon dioxide from air; and it reacts with acids to form the corresponding salts. When boiled for a long time with water, ammonia is evolved; it precipitates hydroxides of silver and copper from soln. of their respective salts; and it liberates ammonia from ammonium salts. H. D. K. Drew and co-workers prepared **palladous dihydroxybispyridine,** $[Pd(C_5H_5N)_2.(OH)_2]$.

According to H. Müller, if palladous tetramminosulphate is treated with barium hydroxide, there separates pale yellow, crystalline **palladous tetramminohydroxide,** $[Pd(NH_3)_4](OH)_2$. The salt fuses above 100°, and then decomposes by deflagration. It dissolves in water, forming a soln. having a strong alkaline reaction. The aq. soln. absorbs carbon dioxide from the atm. The aq. soln. precipitates hydroxides from soln. of copper, iron, cobalt, and nickel salts; and it decomposes ammonium salts. It reacts with acids, forming the corresponding salts. The hydroxide was also prepared by H. D. K. Drew and co-workers. S. Zeisel and A. Nowack observed that when palladous chloride is treated with hydroxylamine hydrochloride and sodium carbonate, there are formed colourless needles of **palladous tetrahydroxylamine hydroxide,**

$$\begin{array}{c} OH \\ \begin{matrix} NH_2OH \\ NH_2OH \end{matrix} \!>\! \overset{\cdot}{\underset{\cdot}{Pd}} \!<\! \begin{matrix} NH_2OH \\ NH_2OH \end{matrix} \\ OH \end{array}$$

in which the two hydroxyl groups are directly attached to the atom of palladium. When this is treated with dil. hydrochloric acid there is formed $[Pd(NH_2OH)_4]Cl_2$, a derivative of the labile base $[Pd(NH_2OH)_4](OH)_2$, in which the hydroxyl groups lie on the second sphere of the molecule. A. Gutbier and M. Woernle prepared **palladous bisethylenediaminohydroxide,** $[Pd\,en_2](OH)_2$; and **palladous bispropylenediaminohydroxide,** $[Pdpn_2](OH)_2$. H. D. K. Drew and co-workers prepared **palladous quaterpyridinohydroxide,** $[Pd(C_5H_5N)_4](OH)_2$.

According to L. Wöhler and F. Martin, **palladium hemitrioxide,** or **palladium sesquioxide,** $Pd_2O_3.nH_2O$, is prepared by the action of ozone on a soln. of palladous nitrate; and better, by the electrolytic oxidation of a soln. of palladous nitrate:

A conc. soln. of palladous nitrate is cooled to 8° and electrolyzed at a current density of 0·5 amp. per cm.[2] until the brown precipitate of the sesquioxide has settled out; the latter, after washing with ice-cold water, is quite pure. If the electrolysis be continued, the dioxide is ultimately obtained, most readily in acidic soln. This is not a direct oxidation, but the sesquioxide decomposes into dioxide and monoxide, the latter then dissolving in the free acid and undergoing further oxidation. In accordance with this view, the sesquioxide is scarcely acted on when electrolyzed in alkaline soln., as the monoxide is insoluble in alkali lye.

The brown hydrated oxide is unstable, and it decomposes under an oxygen press. of 80 atm. at ordinary temp. It is readily soluble in hydrochloric acid, forming an unstable palladium trichloride.

J. J. Berzelius prepared hydrated **palladium dioxide,** $PdO_2.nH_2O$, more or less contaminated with alkali, by treating a soln. of potassium palladate with a slight excess of potassium hydroxide. The brown precipitate is washed with hot water, and dried over conc. sulphuric acid. The product approximates $PdO_2.2H_2O$, or $Pd(OH)_4$. A. Mailfert prepared the hydrated dioxide free from alkali by the action of ozone on a cold soln. of palladous chloride in dil. alkaline soln. The product contained traces of a basic chloride. E. Leidié and L. Quennessen obtained the dioxide by treating spongy palladium with sodium dioxide, but they were unable to isolate the dioxide. L. Wöhler and F. Martin obtained the hydrated dioxide by the anodic oxidation of a nearly neutral soln. of palladous nitrate using nitric acid as cathodic depolarizer. The conc. soln. of palladous nitrate at 8° is electrolyzed with the current density 0·5 amp. per sq. cm. The hydrated sesquioxide is first formed, but by continued electrolysis, the hydrated dioxide is produced—*vide supra.*

G. R. Levi and C. Fontana did not obtain any interference in examining the X-radiograms of the hydrated dioxide. L. Wöhler and J. König observed that the hydrated dioxide is unstable; in contact even with cold water it decomposes slowly into monoxide and oxygen. The dry substance is more stable, but at about 200° it is completely decomposed. Its behaviour towards acids and alkalies varies with the time which has elapsed since its preparation. The substance when dried over sulphuric acid dissolves readily in nitric acid and fairly readily in sulphuric acid. When freshly-precipitated, it is insoluble in a dil. soln. of sodium hydroxide. It is a strong oxidizing agent, and reduces hydrogen dioxide both in acidic and alkaline soln. J. Thomsen gave $(Pd,O_2,2H_2O)=30·43$ Cals. for the heat of formation. Palladium dioxide is reduced by hydrogen at ordinary temp., and so much heat is evolved in the process that the mass becomes incandescent. The subject was discussed by I. Bellucci.

A. Mailfert said that **potassium dipalladite** is formed when ozone acts on palladous oxide in the presence of potassium hydroxide.

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§ 8. Palladium Fluorides

H. Moissan [1] obtained a dark-coloured, crystalline salt by the action of fluorine on palladium at a dull red-heat. The salt decomposes at a bright red-heat leaving palladium behind. O. Ruff observed that the reaction with fluorine and palladium is slow at a red-heat. J. J. Berzelius reported palladous fluoride or **palladium difluoride,** PdF_2, to be formed as a brown precipitate when hydrofluoric acid is added to a conc. soln. of palladous nitrate. The product is sparingly soluble in water, but more soluble in hydrofluoric acid. E. Ascher attempted to prepare palladous fluoride in the dry way. When hydrogen or sulphur dioxide is passed over palladium trifluoride at a suitable temp., a mixture of palladium and palladous fluoride is formed. A similar product is obtained by the action of iodine vapour; bromine vapour at 350° has scarcely any action, and at a higher temp. a molten product is obtained containing bromine and fluorine; chlorine behaves similarly. Palladium acts on the fluoride when heated, forming a violet-brown mass containing palladous fluoride, and hydrochloric acid dissolves the difluoride leaving a little palladium. When hydrogen fluoride is passed over palladous chloride at 500° a yellowish-brown crust containing fluorine is formed, and it hinders the further progress of the reaction; at 600°, only palladium itself is formed. Molten ammonium hydrofluoride acts on palladous chloride yielding an impure fluoride containing much chloride; and at 200°, palladium dichloride is the solid phase in the molten ammonium hydrofluoride. The X-radiograms of the difluoride derived from the trifluoride correspond with a lattice of tetragonal symmetry like those of ferrous, cobaltous and nickelous fluorides. The lattice constants are a=4·92 A., and c=3·38 A.; the axial ratio is $a:c$=1:0·685. There are two mols. in the unit cell, the distance between two Pd-atoms is 2·15 A., the calculated sp. gr. is 5·82, and the observed sp. gr. 5·06. F. Ebert gave similar data.

J. J. Berzelius reported **potassium fluopalladite** to be precipitated when potassium fluoride is added to a soln. of palladous nitrate. The light yellow product is sparingly soluble in water. The corresponding **sodium fluopalladite** was obtained in an analogous manner.

H. Müller prepared **palladous tetramminofluoride,** $[Pd(NH_3)_4]F_2$, by the action

of silver fluoride on an ammoniacal soln. of palladous dichlorodiammine, and evaporating. The colourless crystals are stable in air; easily soluble in water; they attack dry glass; and do not precipitate the difluorodiammine when treated with hydrofluoric acid. He also prepared **palladous difluorodiammine,** $[Pd(NH_3)_2F_2]$, by treating a soln. of the corresponding chloride with an excess of silver fluoride. The spontaneous evaporation of the filtered soln. furnishes crystals, which decompose, giving off ammonia at about 60° or 70°.

E. Ascher, and O. Ruff and E. Ascher prepared **palladium trifluoride,** PdF_3, by the action of fluorine on palladous chloride at 200° to 250°. The preparation can be made in a quartz apparatus, but traces of moisture must be excluded. The product is a black, fine-grained, crystalline powder. It is hygroscopic, but it can be preserved in a desiccator. The rhombic **crystals** have the axial ratios $a:b:c=1{\cdot}35:1:0{\cdot}916$. The lattice constants are $a=7{\cdot}49$ A., $b=5{\cdot}54$ A., and $c=5{\cdot}06$ A. There are four elementary mols. per unit cell. The crystals were studied by W. Nowacki. On the other hand, J. A. A. Ketelaar said that the salt is isomorphous with the corresponding fluorides of aluminium, iron, cobalt, and rhodium. The hexagonal cell has three mols. per unit cell; the cell constants are $a=5{\cdot}05$ A., and $c=7{\cdot}08$ A.; the distance between the fluorine atoms is 2·52 A. E. Ascher, and O. Ruff and E. Ascher gave 5·06 for the **specific gravity,** when the value calculated from the lattice constants is 5·19. The trifluoride is reduced by **hydrogen** at room temp., and the heat evolved raises the mass to incandescence. When heated in **air,** the salt forms the monoxide. Cold **water** produces oxygen, and the reaction is faster in warm water, and black palladous hydroxide is formed. Steam at 100° decomposes the salt completely to palladous hydroxide. The trifluoride reacts with **iodine** with the evolution of heat and the formation of a black product. For the action of iodine, **bromine,** and **chlorine,** *vide supra*. A hot, 40 per cent. soln. of **hydrofluoric acid** dissolves the salt, producing a residue soluble in hydrochloric acid. Conc. **hydrochloric acid** dissolves the fluoride in the cold with the evolution of hydrogen fluoride. There is a detonation when a mixture of the trifluoride and **sulphur** is warmed; there is a smell of sulphur monochloride, and a black residue is produced. When warmed with **hydrogen sulphide,** the mass glows and forms a black sulphide. There is a reaction with **sulphur dioxide,** heat is evolved, and white vapours are produced; the residue is a mixture of palladous fluoride and palladium. Conc., hot **sulphuric acid** decomposes the salt with the evolution of hydrogen fluoride. There is a reaction when the salt is warmed in **ammonia,** the mixture becomes red-hot, ammonium fluoride and palladium are formed. Conc., cold **nitric acid** decomposes the salt with the evolution of hydrogen fluoride and the formation of a brownish-black basic nitrate. Red phosphorus reacts when warmed, the mass becomes red-hot, and a black residue is formed; similarly with **carbon**; and with crystalline **silicon.** The trifluoride burns when warmed with **sodium**; **magnesium** reacts explosively; **aluminium** burns with a white flame; **iron** reacts when heated; and when warmed with **palladium,** palladous fluoride is formed. A 33 per cent. soln. of **sodium hydroxide** reacts vigorously in the cold, forming a brown residue which dissolves in hydrochloric acid with the evolution of chlorine. Molten **sodium carbonate** forms palladous oxide and sodium fluoride.

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§ 9. Palladium Chlorides

According to R. J. Kane,[1] dehydrated palladous chloride melts at a red-heat losing half its chlorine, to form **palladium monochloride, or palladium subchloride,** PdCl. The product furnishes a dark reddish-brown, crystalline mass which deliquesces in air; with water, an aq. soln. of ammonium chloride, potassium iodide or ammonia, the salt is decomposed with the separation of palladium. A. Naumann said that the monochloride is soluble in acetone. The existence of this salt as a chemical individual has not been established.

J. J. Berzelius prepared **palladium dichloride** or **palladous chloride,** $PdCl_2$, by evaporating to dryness a soln. of palladium in aqua regia, and dehydrating the residue by a gentle heat. L. R. von Fellenberg obtained the chloride, as a rose-red sublimate, and a garnet-red mass, by heating palladium sulphide in a current of chlorine; and E. H. Keiser and M. B. Breed obtained it as a sublimate by heating spongy palladium to dull redness in chlorine; the anhydrous chloride can be distilled at a low red-heat in a current of chlorine when it yields a sublimate of deliquescent, dark red, acicular crystals. N. W. Fischer obtained a soln. of the chloride by exposing palladium to hydrochloric acid and air; the process of dissolution is then a slow one. If chlorine be passed into hydrochloric acid in contact with palladium, the metal dissolves quickly to form the dichloride; and if nitric acid be added to the hydrochloric acid, some palladous nitrate is formed. By evaporating the hydrochloric acid soln. over quicklime, the chloride is obtained in reddish-brown, prismatic crystals, which, if free from nitric acid, remain dry. L. N. Vauquelin found that when palladium is dissolved in aqua regia, and the nitric acid removed by repeated evaporation with hydrochloric acid, there remains a brownish-yellow, crystalline mass, which, according to the analyses of R. J. Kane, is the *dihydrate*, $PdCl_2.2H_2O$.

The dichloride obtained by dehydrating the dihydrate is a brownish-black mass; the sublimed salt appears as rose-red, or dark red, acicular crystals; the unsublimed salt is a garnet-red crystalline mass. The dihydrate forms reddish-brown, prismatic crystals. V. M. Goldschmidt said that the crystals are probably rhombohedral. L. Pauling discussed the structure. E. H. Keiser and M. B. Breed gave 2·5 for the sp. gr.; and G. Beck, 4·00 for the sp. gr. at 18°; and 44·4 for the mol. vol. J. J. Berzelius observed that the anhydrous salt fuses without decomposition when gently heated in a glass vessel; when fused in a platinum vessel, it acquires a bluish-green colour by taking up platinum chloride. When strongly heated, chlorine and palladium are formed. F. Puche found that the dissociation begins at 600°, and attains one atm. press. at 920°. S. M. Karim and R. Samuel studied the absorption spectrum; and B. Cabrera and H. Fahlenbrach, the paramagnetism. W. Hampe found that palladium dichloride is very sparingly soluble in ether, but is more soluble in alcohol and in water; both the latter soln. are good electrical conductors. The fused chloride conducts well, and the deposited palladium forms a thread which soon stretches from pole to pole, and as soon as the circuit is complete, the palladium thread glows. E. H. Keiser and M. B. Breed observed that when dichloride is heated in air, chlorine is evolved at 160°, and traces of chlorine are slowly given off even at 100°. When heated in an inert gas like carbon dioxide, chlorine is evolved at 250°. A. Joannis gave for the heat of formation $(Pd,Cl_2)=40{\cdot}48$ Cals. R. Samuel and A. R. Despande studied the absorption spectrum; P. Krishnamurti, the Raman effect; W. D. Treadwell and M. Zürcher, the electrometric titration of the salt; and D. M. Bose, and L. A. Welo and A. Baudisch, the magnetic properties.

According to L. R. von Fellenberg, and R. Böttger, the dichloride is easily reduced when it is heated in a current of **hydrogen,** and F. C. Phillips added that reduction occurs even in the cold. According to A. Merget, G. Gore, W. J. Russell, E. D. Campbell and E. B. Hart, and F. C. Phillips, the aq. soln. absorbs hydrogen rapidly, and this property permits hydrogen to be separated from nitrogen; and

R. Böttger found that the salt in aq. soln. is reduced by hydrogen, and C. Brunner added that it is more easily reduced than is the case with a soln. of the platinum salt; and 0·0005 part of hydrogen can be so detected in a mixture of gases. F. C. Phillips observed that the dil. soln. is completely reduced by hydrogen in 24 hrs. A. Mailfert observed that hydrated palladium dioxide is formed when **ozone** acts on an aq. soln. of the dichloride. The salt is soluble in **water,** forming a yellow or yellowish-brown soln., and, added N. W. Fischer, an excess of water decomposes the salt with the precipitation of an oxychloride.

J. J. Berzelius observed that **palladous trioxydichloride**—according to R. J. Kane, $3PdO.PdCl_2.4H_2O$—is formed when a soln. of palladous chloride is repeatedly evaporated to dryness with water. N. W. Fischer found that when a soln. of palladium in aqua regia is evaporated to dryness, and the soln. treated with water, the yellow soln. soon becomes turbid and deposits a brown basic salt. R. J. Kane noted that basic chlorides are formed when a soln. of palladous chloride is treated with alkali lye. The oxychloride is soluble in dil. acids. R. J. Kane also obtained **palladous hexamminoxychloride,** $PdO.PdCl_2.6NH_3$, which is soluble in hydrochloric acid; and also **palladous diamminotrioxydichloride,** $3PdO.PdCl_2.2NH_3.3H_2O$.

L. N. Vauquelin said that the aq. soln. of palladous chloride is yellow, but when an excess of **hydrochloric acid** is added the solubility increases, and a brownish-red soln. is formed—possibly **hydrochloropalladous acid,** H_2PtCl_4. According to A. Pleischl, and R. Kersting, **hydriodic acid,** or a soln. of **potassium iodide,** gives a black precipitate of palladous iodide when added to soln. of palladous chloride, the precipitate is soluble in an excess of the reagent, and, according to J. L. Lassaigne, 1 part of potassium iodide in 400,000 parts of water gives a brown coloration, and after 20 hrs., a flocculent precipitate. M. Baumann found that 1 part of potassium iodide in 5000 parts of water forms a black precipitate with palladous chloride; in 50,000 parts of water a few black flakes are formed on standing; and in 500,000 parts of water, nothing. No precipitation occurs with **potassium chloride or bromide,** or with **ammonium chloride.** O. Henry, and L. A. Buchner utilized the reaction for separating iodides from bromides and chlorides. F. Müller and A. Riefkohl studied the solubility in a $2N$-soln. of **sodium chloride.**

According to N. W. Fischer, **hydrogen sulphide,** and also **ammonium sulphide,** precipitate dark brown palladium sulphide—1 part of palladium in 10,000 parts of liquid gives a yellow coloration. N. W. Fischer observed that when the soln. of the dichloride is heated with sulphurous acid, the metal is precipitated. F. Wöhler said that a sulphite is formed. G. Sailer observed that **sodium hyposulphite** furnishes palladium sulphide. M. C. Lea found that unlike soln. of ruthenium, iridium, and platinum salts, a soln. of palladium dichloride gives a chocolate-brown precipitate when treated with **tetrathionic acid**; and a soln. of palladous chloride mixed with **sodium thiosulphate** and ammonia is coloured yellow, brown, and finally black.

N. W. Fischer reported that **nitrogen** separated from air by phosphorus and washed, when in contact with a soln. of palladous chloride for a fortnight produces a metallic film on the surface of the liquid. G. Gore said that palladous chloride is slightly soluble in liquid **ammonia.** J. J. Berzelius observed that aq. ammonia added in excess to a soln. of a palladous salt forms a mixture which is yellow at first and afterwards colourless; no blue coloration occurs unless copper is present. N. W. Fischer added that if an excess of ammonia is added to a soln. of the dichloride, the brown precipitate which is formed becomes peach coloured, and the addition of more ammonia dissolves the precipitate—particularly on the application of heat. N. W. Fischer, and H. Rose observed that a soln. of **ammonium carbonate** behaves like aq. ammonia. The precipitate of palladous dichlorodiammine produced by ammonia was examined by L. N. Vauquelin, and C. Claus—*vide infra.* For the action of **hydroxylamine,** *vide infra.* K. Maisch precipitated the metal by soln. of **hydrazine hydrate.** N. W. Fischer observed that **potassium nitrite** precipitates the metal from soln. of the dichloride; and C. Claus made observations

on the subject. P. Jannasch and W. Bettges observed that **hydrazine hydrate** precipitates a mixture of oxides. W. Manchot and A. Waldmüller obtained a complex with **nitric oxide.** According to N. W. Fischer, the metal is precipitated from soln. of its salts by **phosphorus ;** and R. Böttger found that **phosphine** precipitates palladium phosphide, but no phosphide is precipitated from soln. of platinum, rhodium, or iridium salts. E. Fink obtained complexes with **phosphorus trichloride,** namely, **palladous phosphorous octochloride,** $PdCl_2.2PCl_3$, which is decomposed by water; and is soluble in benzene; and **palladous phosphorus pentachloride :** $PdCl_2.PCl_3$, which is decomposed by water, and, according to W. Strecker and M. F. Schurigin, and M. F. Schurigin, it has a constitution $(PdCl_2.PCl_3)_2$. It is soluble in chloroform and benzene, but insoluble in carbon tetrachloride and ligroin. J. J. Berzelius found that **sodium phosphate** gives a light yellow precipitate, and N. W. Fischer said a brown precipitate of a basic chloride is formed. J. J. Berzelius said that **sodium arsenate** gives a light yellow precipitate, and N. W. Fischer said no precipitation occurs with sodium arsenate.

W. Manchot and G. Lehmann observed that the temp. of evolution of the halogen on heating is depressed in the presence of **carbon monoxide,** but no carbonyl chloride is formed ; and W. Manchot observed that dry palladous chloride does not give a sublimate when heated in carbon monoxide at any temp. below redness, whereas at higher temp., the palladous chloride sublimes, and similarly when chlorine is substituted for the carbon monoxide. W. Manchot added that palladium occupies a unique position in the platinum family since it yields no compound with carbon monoxide. The reducibility of palladous chloride in aq. soln. by carbon monoxide points to the existence of such a compound, but the conditions necessary for the production of the primary additive compound are very close to those of its decomposition. Moist palladous chloride is reduced by carbon dioxide at 250°, and reduction is complete at a higher temp. In the absence of water, palladous chloride is not reduced by carbon monoxide, and the addition of carbon monoxide does not occur. On the other hand, E. Fink reported a complex **palladous dicarbonylchloride,** $PdCl_2.2CO$, to be formed which is decomposed by heat ; and **palladous hemitricarbonylchloride,** $2PdCl_2.3CO$, which is decomposed by water and is soluble in carbon tetrachloride. W. Manchot and J. König obtained only palladous carbonylchloride, $PdCl_2.CO$, by the action of carbon monoxide on a soln. of palladous chloride in dry methyl or ethyl alcohol at 0°, or by passing carbon monoxide, charged with the vapour of methyl alcohol, over palladous chloride at ordinary temp. R. Böttger, G. Vulpiers, J. Donau, and G. Gore observed that a soln. of palladous chloride is decolorized and reduced by carbon monoxide precipitating the palladium as a black powder. P. C. E. Potain and R. Drouin found that a soln. of palladous chloride containing 1 part of palladium in 10,000 parts of soln. can be used as a qualitative test for carbon monoxide. The presence of 1 part of this gas in 10,000 parts of air can be recognized by its reducing action when the air is bubbled through the acidulated soln. of the chloride. R. Böttger, G. Vulpiers, J. Donau, and G. Gore noted that a soln. of palladous chloride is reduced by **methane,** and **acetylene,** as well as by **coal gas.** F. C. Phillips observed that soln. of palladium dichloride are quickly reduced by **ethylene ;** and S. C. Ogburn and W. C. Brastow utilized the reaction for the determination of palladium. J. J. Berzelius said that when the soln. of the dichloride is boiled with **alcohol,** the metal is precipitated. W. Eidmann said that the salt is soluble in **acetone ;** and A. Naumann, in **ethyl acetate.** P. Gorceix observed that the acetylacetonate is formed when **acetylacetone** is added in great excess to a soln. of palladous chloride. F. Döbereiner obtained the metal by the action of **sodium formate** in hot soln. According to J. J. Berzelius, **alkali oxalates** give a yellow precipitate of the oxalate, and **oxalic acid** gives a similar precipitate with neutral soln., but at the same time some metal is reduced. J. J. Berzelius observed the formation of pale yellow precipitates with **alkali tartrates and citrates.** W. H. Wollaston found that **potassium cyanide,** or **mercuric cyanide,** produces a yellowish-white, gelatinous

precipitate of palladium cyanide, which becomes white after some time, and is soluble in hydrochloric acid. Observations were made by H. Rose, and H. Rössler. F. Wöhler added that the precipitation is not complete. H. Rose said that no precipitate is formed when **potassium ferrocyanide** is first added to the soln., but after a time a thick jelly is produced; N. W. Fischer added that a yellowish-brown precipitate is formed. C. Claus noted that the precipitation is favoured by heat. H. Rose reported that **potassium ferricyanide** behaves like the ferrocyanide, and A. Smee added that a reddish-brown precipitate is formed, and C. Claus noted that the precipitation is brought about by heat. N. W. Fischer said that **gallic acid** has no effect on soln. of palladous chloride. E. Pace obtained a double salt with **cocaine.** M. C. Lea found that unlike the salts of ruthenium and iridium, palladium chloride gives with **quinine sulphate** a brown precipitate—*vide supra,* the analytical reactions of palladium. C. Claus, and N. W. Fischer found that a soln. of **borax** gives a yellowish-brown precipitate with a soln. of palladous chloride. The precipitation is slow in the cold, but assisted by heat. All the palladium is precipitated.

N. W. Fischer observed that **silver** does not reduce palladium from soln. of its salts, but palladium salt soln. are reduced by all **metals** which reduce silver from soln. of silver salts—**3**. 22, 5. If the palladium be reduced by **tin,** the liquid acquires a brown tint from the presence of a stannous salt, and a brown precipitate is formed; and **mercury** likewise forms a brown precipitate. According to A. Merget, paper impregnated with palladous chloride is a delicate test for the presence of mercury vapour in the atmosphere; the tint of the paper deepens on exposure to mercurial fumes. J. J. Berzelius reported that **potassium** or **sodium hydroxide** precipitates a colourless basic salt, and N. W. Fischer said that the precipitate is dark brown, and that it dissolves when heated with an excess of the precipitant. Observations were also made by C. Claus. N. W. Fischer reported that **sodium** or **potassium carbonate** behaves similarly, and H. Rose added that the soln. in an excess of potassium carbonate becomes dark coloured when boiled, and then gives a brown precipitate, but an excess of sodium carbonate dissolves very little of the precipitate. When a soln. of the palladous salt and alkali is boiled, nearly all the palladium is precipitated as basic palladous carbonate. N. W. Fischer found that soln. of **barium, strontium,** or **calcium hydroxides** behave like soln. of the alkali carbonates. M. C. Lea said that the precipitation with baryta-water is complete and that the precipitate is not soluble in an excess. F. Döbereiner observed that the precipitation with lime-water is incomplete and that the filtrate in sunlight gives a further precipitation of hydrated palladium oxide. H. Rose observed no precipitation with **barium carbonate.** C. Claus observed that **silver nitrate** gives a yellowish-white precipitate. N. W. Fischer found that **mercurous nitrate** gives a yellow or brown precipitate, and in time there is a separation of palladium—a yellow coloration is produced in soln. with 1 part of palladium in 100,000 parts of liquid. W. H. Wollaston said that **stannous chloride** gives a brownish-black precipitate with soln. of palladous chloride, and some palladium is formed at the same time—1 part of palladium can be recognized in 100,000 parts of liquid by this reaction. C. Claus said that **lead acetate** produces a yellow precipitate soluble in excess. W. H. Wollaston found that **ferrous sulphate** reduces a soln. of the chloride to platinum, and N. W. Fischer added that the reaction is slow, particularly if an excess of acid be present—1 part of palladium can be thus recognized in 1000 parts of liquid. O. W. Gibbs observed that no precipitation occurs when **cobaltic hexamminochloride** is added to an acidic soln. of palladous chloride.

L. N. Vauquelin, and N. W. Fischer prepared **palladous dichlorodiammine,** $[Pd(NH_3)_2Cl_2]$, by supersaturating a soln. of palladous chloride with enough ammonia to redissolve the precipitate first formed, and then evaporating the liquor, or treating the soln. with enough hydrochloric acid to precipitate the compound. The product is washed with water, and dried at 100° to 105°.

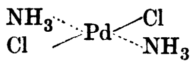
J. J. Berzelius, and H. St. C. Deville and H. Debray also obtained it by evaporating to dryness a soln. of palladous chloride supersaturated with ammonia, or ammonium chloride and extracting the product with water, the dichlorodiammine remains undissolved. H. Fehling obtained it as a precipitate by treating the mother-liquor left in preparing the corresponding chloropalladite with hydrochloric or nitric acid; by heating the chloropalladite; and N. W. Fischer, by dissolving the chloropalladite in ammonia and adding hydrochloric acid. H. Loiseleur obtained the salt by the action of neutral ammonium oxalate on ammonium chloropalladite. The salt was also prepared by H. D. K. Drew and co-workers. A. Gutbier and co-workers recommended the following process:

Purified palladium is dissolved in hydrochloric and nitric acids, and the soln. is evaporated repeatedly on the water-bath with hydrochloric acid. The residue is dissolved in the smallest possible quantity of hydrochloric acid, and the soln. filtered into a platinum basin containing an excess of ammonium hydroxide. By prolonged warming on the water-bath, the precipitated Vauquelin's salt is redissolved. The clear yellow soln. is saturated with hydrogen chloride, and the yellow, crystalline palladoammine chloride washed thoroughly with water. The process of soln. in ammonium hydroxide, reprecipitation by hydrochloric acid and washing, is thrice repeated, and the resulting chloride is dried for 70 hrs. in a vacuum and finally at 105° to 110° to constant weight.

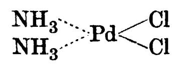
According to H. Dufet, and A. M. Boldyreva, the salt forms yellow, tetragonal prisms. H. Müller described the crystals; and N. S. Kurnakoff discussed the colour of the salt, and he gave 2·5 for the sp. gr. G. Beck gave 2·60 for the sp. gr. at 18°; 81·4 for the mol. vol.; and 187 Cals. for the heat of formation. J. J. Berzelius, and W. A. Lampadius observed that when the salt is heated in a retort, it turns green, and first gives off ammonia, then hydrochloric acid and nitrogen, and finally ammonium chloride, and leaves a residue of porous, grey palladium. F. Isambert gave for the heat of formation $(PdCl_2,2NH_3)=40$ Cals. C. Matignon studied the entropy of the ammino-chlorides. The salt is slightly soluble in water; W. A. Lampadius observed that a sat. soln. at 16° contains 0·26 per cent. of the salt; and H. Müller, 0·304 per cent. H. Baubigny prepared the *monohydrate*, $[Pd(NH_3)_2Cl_2].H_2O$, by treating an alcoholic suspension of the anhydrous salt with conc., aq. ammonia, and evaporating off the ammonia from the mixture on a water-bath. As the soln. cools, some anhydrous chloride, and tetramminochloride first separate, and the monohydrate is then formed by the spontaneous evaporation of the liquid. H. Loiseleur obtained it by the action of neutral ammonium oxalate on ammonium chloropalladite. The yellow, tetragonal prisms of the hydrate were found by H. Baubigny to be soluble in water, and insoluble in alcohol, to effloresce in air, and lose their water of crystallization at 90° thereby forming the sparingly-soluble anhydrous salt. The boiling, aq. soln. deposits the anhydrous chloride; and acids precipitate the anhydrous chloride from the aq. soln.

H. Müller found that when palladous dichlorodiammine is boiled for a long time with a large excess of water, ammonia is given off, and palladous chloride remains. If chlorine is conducted through cold water with the dichlorodiammine in suspension, the salt dissolves, forming a deep red soln. from which ammonia precipitates the tetramminochloropalladate; in hot soln., there is formed successively the tetramminochloropalladate, ammonium chloropalladite, palladous chloride, and palladic chloride. Hot, conc. hydrochloric acid was found by N. W. Fischer to dissolve the dichlorodiammine. According to H. H. Croft, hydrogen sulphide or ammonium sulphide produces a red precipitate which rapidly passes into palladium sulphide. The dichlorodiammine is soluble in sulphurous acid. H. Fehling, and N. W. Fischer observed that it is soluble in cold, aq. ammonia, from which soln. it is precipitated by hydrochloric acid; it is sparingly soluble in hot nitric acid, forming a brown soln. which behaves like a soln. of palladous tetramminochloropalladite. H. Müller observed that the salt is soluble in potash lye, forming a yellow soln. without the evolution of ammonia. H. Schwarz studied some reactions of the salt.

F. Krauss and K. Mählmann observed no evidence of *cis*-, *trans*-, or co-ordination isomerism with the compound $[Pd(NH_3)_2Cl_2]$, but F. Krauss and F. Brodkorb, and A. A. Grinberg and V. M. Shulman had previously reported *cis*- and *trans*-forms. The pink salts obtained by L. N. Vauquelin by the action of ammonia on a palladous salt in aq. soln. have been represented as the *cis*-form, and the yellow salts obtained by H. Müller by dissolving the pink salt in an excess of ammonia and adding a mineral acid has been represented as the *trans*-form.



Symmetrical (Trans)



Unsymmetrical (Cis)

The cis-salt was obtained, as a yellow powder, by A. A. Grinberg and V. M. Shulman, by the action of ammonium acetate on potassium chloropalladite; and potassium iodide gives a red coloration with acetone soln. of the *cis*-compound, but not so with the *trans*-isomeride.

There is a form of the dichlorodiammine which occurs as a yellow microcrystalline powder, and in salmon-pink minute crystals. Both forms are so sparingly soluble in liquids that determinations of the molecular weights are made with difficulty. H. D. K. Drew and co-workers showed that the yellow compound is the true diamminodichloride, $[Pd(NH_3)_2Cl_2]$, and that the pink compound is palladium tetramminochloropalladite, $[Pd(NH_3)_4]PdCl_4$, and therefore the *cis-trans* isomerism does not arise. F. G. Mann and co-workers, examined some deep red crystals sometimes obtained by R. H. Atkinson, by drying the yellow form at 200°. The chemical properties of the red and yellow forms appeared to be identical; both forms in saturated acetone soln. give a faint yellow coloration with potassium iodide, which is not the case with the *cis*-salt of A. A. Grinberg and V. M. Shulman. The facts show that the yellow powder and the red crystals have the *trans*-configuration, and the crystallographic evidence leaves little room for doubting, but their difference is due essentially to different crystal structures built up from the same *trans*-molecules. T. M. Lowry, H. D. K. Drew and co-workers showed that the red and yellow salts are not isomeric diammines. The pink salts are the palladium analogues of Magnus' platinum salts, $[Pd(NH_3)_4]PdCl_4$; whilst the yellow compounds are monomeric, and, as first shown by N. S. Kurnakoff, and by A. Gutbier and co-workers, they correspond with $[Pd(NH_3)_2Cl_2]$. The subject was studied by A. Rosenheim and L. Gerb, F. P. Dwyer and D. P. Mellor, and F. W. Pinkard and co-workers.

W. A. Burdakoff prepared **platinous dichlorohydrazine,** $[Pd(N_2H_4)Cl_2]$, as a yellowish-white precipitate, partly hydrolyzed by cold water, and completely by boiling water: $3Pd(N_2H_4)Cl_2 = 3Pd + 2NH_4Cl + 4HCl + 2N_2$. S. Zeisel and A. Nowak obtained **palladous dichlorodihydroxylamine,** $[Pd(NH_2OH)_2Cl_2]$, by treating the tetrahydroxylaminohydroxide—*vide supra*—with a small proportion of dil. hydrochloric acid; the precipitate appears in slender, yellow needles, and as a yellow, granular powder. The compound is too unstable to permit a close examination of its characteristics. F. Krauss and F. Brodkorb prepared cis- and trans-forms.

A. Rosenheim and T. A. Maass, H. D. K. Drew and co-workers, A. Gutbier and M. Woernle, and A. Gutbier and A. Krell prepared **palladous dichlorobispyridine,** by adding pyridine to an aq. soln. of palladous chloride, or potassium chloropalladite. The red precipitate dissolves on heating with an excess of pyridine, and conc. hydrochloric acid precipitates from the soln. a bright yellow, crystalline powder. If heated with ammonia the pyridine is displaced, and the dichlorodiammine is formed. F. Krauss and F. Brodkorb obtained cis- and trans-forms. A. Rosenheim and T. A. Maass, and A. Gutbier and A. Krell prepared the corresponding **palladous dichlorobisquinoline,** $[Pd(C_9H_7N)_2Cl_2]$, in a similar manner by using quinoline in place of pyridine. The yellow precipitate which is formed is soluble in ammonia. By treating an aq. soln. of potassium chloropalladite with benzylamine, a red precipitate is formed, and this dissolves in an excess of the base to furnish a colourless soln., which, on the addition of conc. hydrochloric acid, yields yellow, crystalline leaflets of **palladous dichlorobisbenzylamine,** $[Pd(C_6H_5.CH_2NH_2)_2Cl_2]$, A. Rosenheim and L. Gerb discussed the optical isomerism

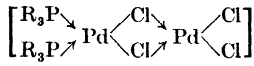
of the complex salts of bivalent palladium. H. D. K. Drew and co-workers prepared **palladous dichloroethylenediamine,** [$Pd\,enCl_2$], in orange-yellow, rectangular needles. N. S. Kurnakoff and N. J. Gwosdareff prepared this compound and also **palladous dichlorobisethylenediamine,** $Pd\,en_2Cl_2$; and the crystals were studied by E. G. Cox and G. H. Preston, and found to be isomorphous with those of the corresponding platinous salt. I. L. Kondakoff and co-workers prepared **palladous trimethylethyleneochloride.** A. Gutbier and co-workers prepared **palladous dichlorobis-isopropylamine,** [$Pd(C_3H_7.NH_2)_2Cl_2$], as a pale yellow, crystalline powder; **palladous dichlorobisdipropylamine,** [$Pd\{(C_3H_7)_2NH\}_2Cl_2$], in pale yellow crystals; **palladous dichlorobis-n-butylamine,** [$Pd(C_4H_9NH_2)_2Cl_2$], as a pale yellow, crystalline powder; **palladous dichlorobisdi-iso-butylamine,** [$Pd\{(C_4H_9)_2NH\}_2Cl_2$], in pale yellow plates; **palladous dichlorobis-iso-amylamine,** [$Pd(C_5H_{11}.NH_2)_2Cl_2$], in pale yellow plates; **palladous dichlorobisdi-iso-amylamine,** [$Pd\{(C_5H_{11})_2NH\}_2Cl_2$], in pale yellow needles; W. L. Hardin, and A. Gutbier and co-workers, **palladous dichlorobisphenylamine,** $PdCl_2(C_6H_5NH_2)_2$. A. Gutbier and co-workers, **palladous dichlorobistolylamine,** $PdCl_2(C_7H_7NH_2)_2$, in its *o*- and *p*-forms; **palladous dichlorobioxylylamine,** $PdCl_2\{C_6H_3(CH_3)_2NH_2\}_2$; **palladous dichlorobis-p-anisylamine,** $PdCl_2\{C_6H_4(OCH_3)NH_2\}_2$; **palladous dichlorobis-α-naphthylamine,** $PdCl_2(C_{10}H_7.NH_2)_2$; **palladous dichlorobis-β-naphthylamine; palladous dichlorobisbenzidylamine,** $PdCl_2.C_{12}H_8(NH_2)_2$; **palladous dichlorobis-o-phenylenediamine,** $PdCl_2.C_6H_4(NH_2)_2$; L. Gerb, and A. Rosenheim and L. Gerb, **palladous dichlorotoluyldiamine;** A. Rosenheim and W. Händler, **palladous dichlorobis-iso-butylenediamine; palladous dichlorobismethylphenylamine,** $Pd\{(CH_3)(C_6H_5)NH\}_2Cl_2$; **palladous dichlorobisethylphenylamine,** $Pd\{(C_2H_5)(C_6H_5)NH\}_2Cl_2$; **palladous dichlorobisbenzalaniline,** [$Pd(C_6H_5.CH : N.C_6H_5)_2Cl_2$], in greyish-yellow plates; **palladous dichlorobis-o-nitraniline,** [$Pd(C_6H_5.NO_2.NH_2)_2Cl_2$], as a yellow, crystalline powder; **palladous dichlorobis-m-nitraniline,** in pale yellow crystals; **palladous dichlorobis-p-nitraniline,** as golden-yellow, crystalline powder; A. Gutbier and co-workers obtained **palladous dichlorobenzylchloroamine,** $Pd\{(CH_2.C_6H_5Cl.NH_3\}_2Cl_2$; **palladous dichlorodibenzylchloroamine,** $Pd\{(CH_2.C_6H_5)_2Cl.NH_2\}_2Cl_2$; **palladous dichlorobenzylamine,** $Pd\{(CH_2)(C_6H_5)NH_2\}_2Cl_2$; **palladous dichlorobis-2-methylpyridine,** $Pd[C_5H_4(CH_3)_2Cl_2]$; W. L. Hardin, **palladous dichlorobisquinoline,** $Pd(C_9H_7N)_2Cl_2$; and **palladous dichlorobispiperidine,** $Pd(C_5H_{11}N)_2Cl_2$; **palladous dichlorobis-1.2.3-xylidine,** [$Pd\{C_6H_3(CH_3)_2NH_2\}_2Cl_2$], in golden-yellow needles; **palladous dichlorobis-1.3.4-xylidine,** in golden-yellow crystals; **palladous dichlorobis-1.4.5-xylidine,** in golden-yellow crystals; **palladous dichloro-1.3.4-bistolulyenediamine,** [$Pd\{C_6H_3.CH_3(NH_2)_2\}Cl_2$], in dark brown plates; **palladous dichlorobis-p-phenetidine,** [$Pd(C_6H_4.O.C_2H_5.NH_2)_2Cl_2$], as a yellow, microcrystalline powder; **palladous dichlorobispicoline,** [$Pd(C_5H_4.CH_3.N)_2Cl_2$], as pale yellow crystals, in its α- and β-forms; **palladous dichlorobislutidine,** [$Pd\{C_5H_3(CH_3)_2N\}_2Cl_2$], as a yellow, crystalline powder; **palladous dichlorobiscollidine,** [$Pd\{C_5H_2(CH_3)_3N\}_2Cl_2$], in dark yellow crystals; **palladous dichlorobispiperidine,** [$Pd(C_5H_{10}.NH)_2Cl_2$], in yellow crystals; and **palladous dichlorobis-iso-quinoline,** [$Pd(C_9H_7.N)_2Cl_2$], in yellow needles. F. G. Mann and W. J. Pope prepared **palladous ββ′ ββ″ triaminotriethylaminchloropalladate,** [$PdN(C_2H_4.NH_2)_3]PdCl_6.H_2O$; and E. Dreschel, **palladous dichlorobiscarbamide,** [$Pd\{NH_2(CO.NH_2\}_2Cl_2$]. E. G. Cox and co-workers prepared a complex **palladous disalicylaldoximinochloride.**

E. C. Fritzmann, E. G. Cox and co-workers, L. Tschugaeff and C. Ivanoff, and H. D. K. Drew and G. H. Wyatt, described **palladous dichlorobisdiethylsulphine,** [$Pd\{(C_2H_5)_2S\}_2Cl_2$]; and **palladous dichloro-bis-methylethylsulphine,** [$Pd(CH_3SC_2H_5)_2Cl_2$]; **palladous dichloroethylenebisdiethylsulphine,** [$Pd\{S(C_2H_2).CH_2.C_2H_5.S(C_2H_5)\}Cl_2$]; **palladous dichlorobismethylselenine,** $PdCl_2.2(CH_3)_2Se$; **palladous dichlorobisethylselenine,** $PdCl_2.2(C_2H_5)_2Se$; **palladous dichlorobispropylselenine,** $PdCl_2.2(C_3H_7)_2Se$; **palladous dichlorobisbutylselenine,** $PdCl_2.2(C_4H_9)_2Se$; **palladous dichlorobispentylselenine,** $PdCl_2.2(C_5H_{11})_2Se$; **dichlorobisphenylselenine,** $PdCl_2.2(C_6H_5)_2Se$; and **palladous dichlorodiethyltrimethyleneselenide,** $PdCl_2(C_2H_5)Se$-$(CH_2)_3Se(C_2H_5)$. G. T. Morgan and V. E. Yarsley obtained **palladous trimethylstibinochloride,** [$Pd\{(CH_3)_3Sb\}_4Cl_2$], and [$Pd\{(CH_3)_3Sb\}_2Cl_2$].

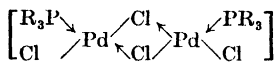
E. Fink prepared **palladous dichlorobismethylphosphite,** $\{P(OCH_3)_3\}_2PdCl_2$; **palladous dichlorobisethylphosphite,** $\{P(OC_2H_3)_3\}_2PdCl_2$; **palladous dichlorodiamminomethylphosphite,** $\{P(OCH_3)_3(NH_3)_2PdCl_2$; **palladous dichlorodiamminoethylphosphite,** $\{P(OC_2H_5)_3\}(NH_3)_2PdCl_2$; **palladous dichlorotoluidinomethylphosphite,** $\{P(OCH_3)_3\}(C_7H_9N)PdCl_2$; **palladous dichlorotoluidinoethylphosphite,** $\{P(OC_2H_5)_3\}(C_7H_9N)PdCl_2$; **palladous dichloropyridinomethylphosphite,** $\{P(OCH_3)_3\}(C_5H_5N)PdCl_2$; **palladous dichloropyridinoethylphosphite,** $\{P(OC_2H_5)_3\}(C_5H_5\}N)$-$PdCl_2$; **palladous dichloroamidobismethylphosphite,** $Pd\{P(OCH_3)_3\}_2(NH_2)_2(HCl)_2$; and **palladous chloroamidobisethylphosphite,** $P_2O(OC_2H_5)_2Pd(NH_2)HCl$. F. D. Mann and D. Purdie prepared homologous members of the three series **palladous disulphinodichloride,** [$(R_2S)_2PdCl_2$]; **palladous diphosphinodichloride,** [$(R_3P)_2PdCl_2$]; and **palladous diarsinodichloride,** [$(R_3As)_2PdCl_2$]. The palladous diphosphinodichloride, [$Pd(PR_3)_2Cl_2$], occurs in the stable form as the *trans*-isomeride

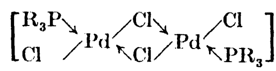
$$\left[\begin{array}{ccc} R_3P\searrow & & \swarrow Cl \\ & Pd & \\ Cl\nearrow & & \searrow PR_3 \end{array}\right]$$

the **palladous monophosphinodichloride**, $[Pd(PR_3)Cl_2]_2$, is formed when the preceding compound is boiled with ammonium chloropalladite, $(NH_4)_2PdCl_4$. The general reactions of the compound favour the formula



The monophosphinodichloride furnishes an isomeride which has one of the two following constitutions :





The arsino-compounds also yield **palladous mono-arsinodichloride.**

H. Müller prepared **palladous tetramminochloride,** $[Pd(NH_3)_4]Cl_2$, by the action of dry ammonia on dry palladous chloride, or dichlorodiammine. The white product loses ammonia in vacuo, to form the dichlorodiammine. The dissociation press. is 760 mm. at 210°. The crystals of this salt, the palladium analogue of Magnus' green salt, were found by E. G. Cox and co-workers to be similar in appearance and to have a similar X-radiogram to that of the platinum salt. The colourless prisms of the monohydrate are isomorphous with the corresponding platinum compound ; they are tetragonal combinations of (100) and (111). The cell dimensions are $a=14{\cdot}30$, and $c=4{\cdot}27$ A. ; there are 4 mols. per unit cell ; and the calculated sp. gr. is 2·01, when the observed value is 1·94. According to B. N. Dickinson, the salt $Pd(NH_3)_4Cl_2.H_2O$, has a simple tetragonal lattice with $a=10{\cdot}322$ A., and $c=4{\cdot}34$ A. The interatomic distances are Pd to N, 2·02 A. ; Cl to H_2O, 3·81 A. ; H_2O to NH_3, 3·16 A. ; Cl to NH_3, 3·44 A. ; NH_3 to NH_3, in the same cation, 2·86 A., and in different cations, 4·06 A. There are two molecules per unit cell. The corresponding platinous salt has a similar structure. G. Beck gave 1·91 for the sp. gr. at 18° ; 128·5 for the mol. vol. ; and 362 Cals. for the heat of formation. F. Isambert gave for the heat of formation $[Pd(NH_3)_2Cl_2]+2NH_3=[Pd(NH_3)_4]Cl_2+31{\cdot}12$ Cals. H. Fehling, H. Müller, and H. Baubigny prepared the *monohydrate*, $[Pd(NH_3)_4]Cl_2.H_2O$, by dissolving the dichlorodiammine in a soln. of ammonia and ammonium chloride, and concentrating the soln. by evaporation. The colourless prisms were found by A. M. Boldyreva to be tetragonal and uniaxial. N. S. Kurnakoff discussed the colour of the salt. The salt is very soluble in water, and loses ammonia and water at 120°, re-forming the dichlorodiammine. Acids added to the aq. soln. precipitate the anhydrous dichlorodiammine ; and, according to R. J. Kane, potassium hydroxide forms a brownish-green precipitate which detonates violently when dried.

L. N. Vauquelin obtained **palladous tetramminochloropalladite,** $[Pd(NH_3)_4]PdCl_4$, in the course of his work on the platinum ores, and he prepared the salt—*Vauquelin's red salt*—by adding a slight excess of ammonia to a moderately conc. soln. of palladous chloride. H. Fehling employed a similar process, and H. Müller obtained it by adding palladous chloride to the tetramminochloride. The salt was also prepared by H. D. K. Drew and co-workers. L. N. Vauquelin, and H. Fehling observed that the rose-red scales or prismatic needles, when moist, form the yellow isomeric dichloro-diammine at 100° ; but the dry salt retains its colour at 180°, and at 200°, it is transformed into yellow dichlorodiammine without losing weight ; at a higher temp. it fuses, gives off gas, and leaves a residue of palladium. G. Beck studied the ionization of the palladium ammines. W. N. Fischer, and H. Fehling found that the salt is insoluble in cold water, and it dissolves in boiling water with decomposition, leaving a brown residue. A small proportion of water at 100° furnishes the yellow dichlorodiammine. The cooling of the hot aq. soln. or the addition of hydrochloric or nitric acid also furnishes the dichlorodiammine, L. N. Vauquelin observed that the salt dissolves slowly in cold, dil. hydrochloric acid, rapidly when heated, forming the ammonium salt. When ammonia is added

to the soln. in nitric acid, the tetramminochloropalladite is re-precipitated; if the nitric acid soln. be evaporated to dryness, palladous nitrate, and an ammonium salt are formed. The tetramminochloropalladite dissolves slowly in boiling aq. ammonia, and acids precipitate from the soln. the yellow dichlorodiammine. H. Schwarz studied some reactions of the salt.

H. St. C. Deville and H. Debray, and H. H. Croft prepared **palladous tetramminochloropalladate,** $[Pd(NH_3)_4]PdCl_6$, by the action of chlorine on a cold, aq. soln. of palladous dichlorodiammine, or by the action of aqua regia on the tetramminochloride. H. St. C. Deville and H. Debray thought the product had the composition $PdCl_3.2NH_3$. The compound is brownish-black, and crystalline. When heated, it melts and decomposes to furnish hydrogen chloride, nitrogen, ammonium chloride, and spongy palladium. Boiling water decomposes it to form ammonium chloropalladite and nitrogen; and an excess of aq. ammonia dissolves it to form the tetramminochloride. S. Zeisel and A. Nowak prepared colourless crystalline **palladous tetrahydroxylaminochloride,** $[Pd(NH_2OH)_4]Cl_2$, by the action of dil. hydrochloric acid on the hydroxide—*vide supra.* A. Rosenheim and T. A. Maass said that the product obtained by the action of chlorine water in the cold on palladous dichlorodiammine is really a mixture containing for the most part ammonium chloropalladate, and at a higher temp. ammonium chloropalladite is produced. Yellow and red compounds have been prepared, but neither cis-, trans-, nor co-ordination isomerism exists. T. Wilm prepared **palladous chloropentammine chloromercurite,** $[Pd(NH_3)_5Cl](HgCl_3)_2$. F. Krauss and K. Mählmann found that both varieties, in aq. suspension, with chlorine yield $[Pd(NH_3)_4]PdCl_6$, and this, when boiled with water, yields chlorine and the yellow diammine, whereas if $[Pd(NH_3)_4]Cl_2$ be treated with potassium chloromercurate, chloro-osmic acid, or picric acid, the corresponding **palladium dichlorodiamminochloromercuriate,** $[Pd(NH_3)_2Cl_2]HgCl_4$; **palladium dichlorodiamminochlorosmate,** $[Pd(NH_3)_2Cl_2]OsCl_6$; or **palladium dichlorodiamminopirate,** is formed. On the other hand, a hydrochloric acid soln. of chloropalladous acid, H_2PdCl_4, yields either the yellow- or rose-form according to the conc. of the hydrochloric acid. Both compounds are considered to be bimolar, and the two forms bear a pseudomonotropic relation to one another. The rose form is the more labile.

A. Gutbier and M. Woernle, and H. D. K. Drew and co-workers prepared **palladous bisethylenediaminochloride,** $[Pd\,en_2]Cl_2$, in pale yellow crystals, by substituting ethylenediamine for ammonia in the preparation of the ammines; they also prepared **palladous bispropylenediaminochloride,** $[Pdpn_2]Cl_2$, in a similar manner. L. Tschugaeff obtained an optically active form. H. Reihlen and W. Hühn obtained complexes of the type **palladous αβ-isobutylenediaminochloropalladite,** $[Pd\{C_4H_8(NH_2)_2\}_2][Pt(\text{or }Pd)Cl_4]$. H. D. K. Drew and co-workers prepared **palladous quaterpyridinochloride,** $[Pd(C_5H_5N)_4]Cl_2.3H_2O$; **palladous bispyridinodiamminochloride,** $[Pd(C_5H_5N)_2(NH_3)_2]Cl_2$, and also the *monohydrate*; **palladous ethylenediaminodiamminochloride,** $[Pd\,en(NH_3)_2]Cl_2$; and **palladous ethylenediaminobispyridinochloride,** $[Pd\,en(C_5H_5N)_2Cl_2$; A. Gutbier and A. Krell, **palladous bisdibenzylaminodichloride,** $Pd\{NH(CH_2.C_6H_5)_2\}_2Cl_2$.

H. D. K. Drew and co-workers prepared **palladous quaterpyridinochloropalladite,** $[Pd(C_5H_5N)_4]PdCl_4$; **palladous bisethylenediaminochloropalladite,** $[Pd\,en_2]PdCl_4$; **palladous bispyridinodiamminochloropalladite,** $[Pd(C_5H_5N)_2(NH_3)_2]PdCl_4$; and **palladous ethylenediaminodiamminochloropalladite,** $[Pd\,en(NH_3)_2]PdCl_4$. A. Gutbier and C. Fellner prepared **palladous quater-iso-propylaminochloropalladite,** $[Pd(C_3H_7.NH_2)_4]PdCl_4$; **palladous quater-n-butylaminochloropalladite,** $[Pd(C_4H_9.NH_2)_4]PdCl_4$; and **palladous quater-iso-amylaminochloropalladite,** $[Pd(C_5H_{11}NH_2)_4]PdCl_4$. N. S. Kurnakoff prepared **palladous quaterthiocarbamidochloride,** $[Pd\{CS(NH_2)_2\}_4]Cl_2$; and K. A. Jensen, **palladous thiocarbazidochloride,** $[Pd(thio)_2]Cl_2$, and $[Pd(thio)Cl_2]$.

J. Thomsen represented the heat of formation of **hydrochloropalladous acid,** H_2PdCl_4, by $(Pd,O,4HCl,Aq.)=37{\cdot}64$ Cals.; $(Pd(OH)_2,4HCl,Aq.)=14{\cdot}93$ Cals.; and $(Pd,Cl_2,2HCl,Aq.)=47{\cdot}92$ Cals. W. H. Wollaston obtained **potassium chloropalladite,** K_2PdCl_4, from a soln. of palladium in hydrochloric acid mixed with nitre; and J. J. Berzelius, by adding potassium chloride to a soln. of palladous chloride—with conc. soln., the salt is precipitated in golden-yellow needles, but dil.

soln. must be first concentrated by evaporation. W. H. Wollaston, and H. Rössler obtained the salt by igniting the chloropalladate out of contact with air. The four-sided prisms, said W. H. Wollaston, appear red by light transmitted along the axis, and light green in all other directions, but J. J. Berzelius stated that the greenish-brown prisms are not dichroic. According to C. Bodewig, the crystals are isomorphous with those of the corresponding chloroplatinite; the similarity of the crystal forms was noted by W. H. Wollaston. R. G. Dickenson also noted that the crystals are isomorphous with those of the corresponding platinum salt; and that the X-radiograms correspond with a tetragonal lattice having the parameters $a=6{\cdot}99$ A., and $c=4{\cdot}13$ A. The calculated density is 2·66. W. Jander, and L. Pauling and M. L. Huggins made some observations on the lattice structure. According to J. J. Berzelius, E. Biewend, and H. Rössler, the crystals are difficult to dry completely; they retain water above 100°; at 105°, they lose chlorine as hydrogen chloride; they melt at a higher temp., during the fusion a little chlorine is lost, and a little palladium is formed; the salt is completely decomposed at a red-heat, forming palladium and potassium chloride. J. Thomsen gave for the heat of formation, $(Pd,Cl_2,2KCl)=52{\cdot}67$ Cals.; F. Puche, 52·67 Cals.; A. Joannis gave $(PdCl_{2solid},2KCl_{soln.})=K_2PdCl_{4solid}+9{\cdot}32$ Cals., and $(PdCl_{2solid},2KCl_{soln.})=K_2PdCl_{4soln.}+4{\cdot}72$ Cals.; and J. Thomsen gave for the heat of soln., $-13{\cdot}63$ Cals. R. Samuel and co-workers studied the absorption spectrum. H. Rössler observed that the salt is easily reduced by hydrogen. For the oxidation of this salt to K_2PdCl_6, *vide infra*. W. H. Wollaston observed that it readily dissolves in water, forming a dark red soln., and that chlorine converts it into the chloropalladate; J. J. Berzelius, that it is easily reduced by boiling with sulphurous acid, and that ammonia in excess transforms it into palladous dichlorodiammine; W. H. Wollaston, that it is insoluble in alcohol; and J. J. Berzelius, that it dissolves in alcohol of sp. gr. 0·84, but is very sparingly soluble in absolute alcohol, so that the addition of alcohol to the hot, sat. soln. precipitates the salt in golden-yellow plates. L. Wöhler and F. Martin found that in the attempts to prepare salts of tervalent palladium, potassium chloropalladite, $2KCl.PdCl_2$, and **potassium hexachloropalladite,** $4KCl.PdCl_2$, or K_4PdCl_6, are formed. A. Rosenheim and H. Itzig prepared **ammonium trichlorosulphitopalladite,** $(NH_4)_3PdCl_3(SO_3).H_2O$, in red, hexagonal crystals with the axial ratio $a:c=1:0{\cdot}8923$.

According to R. Godeffroy, L. Wöhler and F. Martin, and A. Gutbier and A. Krell, **rubidium chloropalladite,** Rb_2PdCl_4, in light brown needles, is precipitated by adding rubidium chloride to a soln. of palladous chloride and crystallizing the product from its soln. in hot water. They also prepared **cæsium chloropalladite,** Cs_2PdCl_4, in an analogous manner in light brown needles. W. H. Wollaston obtained **ammonium chloropalladite,** $(NH_4)_2PdCl_4$, by crystallization from a mixed soln. of ammonium and palladous chlorides. N. W. Fischer added that the soln. should contain an excess of acid, and he obtained the salt by evaporating a soln. of palladous tetramminochloropalladite in hydrochloric acid. The salt was also prepared by T. Wilm, and A. Gutbier and A. Krell. W. H. Wollaston, and L. N. Vauquelin said that the yellowish-green, four-sided or six-sided prisms and needles exhibit a peculiar play of colours, and R. J. Kane added that the crystals have a bronze lustre. R. G. Dickenson found that the X-radiograms correspond with a tetragonal lattice having $a=7{\cdot}21$ A., and $c=4{\cdot}26$ A., and a calculated sp. gr. of 2·12. This is in agreement with the observations of E. G. Cox and G. H. Preston. L. Pauling and M. L. Huggins discussed the subject. All the water can be expelled by the careful application of heat. W. H. Wollaston, and N. W. Fischer found that salt is easily soluble in water, forming a dark red, or yellowish-brown liquid; and it is insoluble in alcohol, but slightly soluble in aq. alcohol. E. F. Smith and H. F. Keller passed hydrogen sulphide over the salt, at 70° to 80°, and found that it becomes black; at higher temp., some ammonium chloride volatilizes, and a residue, probably of palladous sulphide, remains.

W. L. Hardin prepared **ethylammonium chloropalladite,** $(NH_3.C_2H_5)_2PdCl_4$; A. Gutbier and co-workers prepared **tetramethylammonium chloropalladite,** $\{(CH_3)_4N\}_2PdCl_4$, in dark brownish-red crystals; **iso-propylammonium chloropalladite,** $\{(C_3H_7)NH_3\}_2PdCl_4$, in brownish-red crystals; **n-butylammonium chloropalladite,** $\{(C_4H_9)NH_3\}_2PdCl_4$, in reddish-brown plates; **di-iso-butylammonium chloropalladite,** $\{(C_4H_9)_2NH_2\}_2PdCl_4$, in rose-red plates; **allylammonium chloropalladite,** $\{(C_3H_5)NH_3\}_2PdCl_4$, in brownish-red crystals; **iso-amylammonium chloropalladite,** $\{(C_5H_{11})NH_3\}_2PdCl_4$, in reddish-brown crystals; **di-iso-amylammonium chloropalladite,** $\{(C_5H_{11})_2NH_2\}_2PdCl_4$, in brownish-red crystals; **tri-iso-amylammonium chloropalladite,** $\{(C_5H_{11})_3NH\}_2PdCl_4$, in reddish-brown crystals; **pyridinum chloropalladite,** $(C_5H_6N)PdCl_4$; **guanidinium chloropalladite,** $\{C.NH.(NH_2)_2.H\}_2PdCl_4$, in dark reddish-brown plates.

A. Gutbier and co-workers prepared some compounds of the type $(RCl)_2PdCl_2$—*e.g.* **anilinium chloropalladite,** $(C_6H_5NH_3)_2PdCl_4$; **toluidinium chloropalladite,** $(C_7H_7NH_3)_2.PdCl_2$, in its *o*- and *p*-forms; **methylanilium-chloropalladite,** $PdCl_2\{NH_2(CH_3)(C_6H_5)Cl\}_2$; **ethylaniliniumchloropalladite,** $PdCl_2\{NH_2(C_2H_5)(C_6H_5)Cl\}_2$; and **diethylanilinium chloropalladite,** $PdCl_2\{NH(C_2H_5)_2(C_6H_5)Cl\}_2$; **benzylanilinium chloropalladite,** $(C_6H_5.CH_2.NH_2.C_6H_5)_2.PdCl_4$, in yellowish-brown crystals; **o-chloroanilinium chloropalladite,** $(C_6H_4Cl.NH_3)_2PdCl_4$, in dark orange-red crystals; **m-chloroanilinium chloropalladite,** in pale brown plates; **p-chloroanilinium chloropalladite,** in dark orange plates; **o-nitroanilinium chloropalladite,** $(C_6H_4.NO_2.NH_3)_2PdCl_4$, in brown crystals; **m-nitroanilinium chloropalladite,** in pale brown plates; **p-nitroanilinium chloropalladite,** in dark brown plates; **tribenzylammonium chloropalladite,** $\{(C_6H_5.CH_2)_3NH\}_2PdCl_4$; **dimethyl-o-toludinium chloropalladite,** $\{C_6H_4.CH_3.NH_2.(CH_3)_2\}_2PdCl_4$, in reddish-brown crystals; **xylidinium-1.2.4-chloropalladite,** $C_6H_3(CH_3)_2NH_3\}_2.PdCl_4$, in pale brown needles; **xylidinium-1.3.4-chloropalladite,** in brown needles; **xylidinium-1.4.5-chloropalladite,** in deep brown needles; **p-anisidinium chloropalladite,** $\{C_6H_4(OCH_3)NH_3\}_2.PdCl_4$; **α-naphthylamine chloropalladite,** $(C_{10}H_7NH_3)_2PdCl_4$; **β-naphthylamine chloropalladite,** $(C_{10}H_7NH_3)_2PdCl_4$; **benzidine chloropalladite,** $C_{12}H_8(NH_3)_2PdCl_4$; N. S. Kurnakoff and N. J. Gwosdareff, **ethylenediamine chloropalladite,** $C_2H_4(NH_3)_2.PdCl_4$; A. Gutbier and co-workers, **m-phenylene diamine chloropalladite,** $C_6H_4(NH_2)_2.PdCl_4$; **pseudocumidinium chloropalladite,** $\{C_6H_2(CH_3)_2NH_3\}_2PdCl_4$, as a brown, crystalline powder; **tolylenediammonium-1.2.4-chloropalladite,** $\{C_6H_3.CH_3(NH_3)_2\}PdCl_4$, as a brown, crystalline powder; **methyldiphenylammonium chloropalladite,** $\{(C_6H_5)_2NH.CH_3\}_2PdCl_4$, in dark brown plates; **o-phenetidinium chloropalladite,** $(C_6H_4.O.C_2H_5.NH_3)_2PdCl_4$, in brownish-grey plates; **p-phenetidinium chloropalladite,** in dark brown crystals; **picolinium chloropalladite,** $(C_3H_4.CH_3.NH)_2PdCl_4$, in dark brownish-red crystals, in its α- and β-forms; **lutidinium chloropalladite,** $\{C_5H_3(CH_3)_2NH\}_2PdCl_4$, in dark red plates; **collidinium chloropalladite,** $\{C_5H_2(CH_3)_3NH\}_2PdCl_4$, in dark red crystals; **piperidinium chloropalladite,** $(C_5H_{10}.NH_2)_2PdCl$; in dark reddish-brown crystals; **iso-quinolinium chloropalladite,** $(C_9H_7.NH)_2PdCl_4$, as a pale red crystalline powder.

W. H. Wollaston prepared **sodium chloropalladite,** Na_2PdCl_4, from a mixed soln. of the component chlorides, in red, deliquescent prisms, very soluble in water, easily soluble in alcohol. N. S. Kurnakoff obtained dark yellow crystals of **copper tetramminochloropalladite,** $Cu(NH_3)_4PdCl_4$, by mixing soln. of copper chloride and platinous tetramminochloride; the salt is decomposed by water, and by hydrochloric acid. P. A. von Bonsdorff likewise obtained **calcium chloropalladite,** $CaPdCl_4$, in yellowish-brown, deliquescent needles, soluble in water and alcohol; **barium chloropalladite,** $BaPdCl_4$, in brown crystals easily soluble in water and dil. alcohol; A. Welkow, **beryllium chloropalladite,** $BePdCl_4.6H_2O$, in deep brown, hygroscopic crystals soluble in water and alcohol; P. A. von Bonsdorff, **magnesium chloropalladite,** $MgPdCl_4$, in brown deliquescent, prismatic needles, soluble in water and alcohol; **zinc chloropalladite,** $ZnPdCl_4$, in chestnut-brown, deliquescent needles; **cadmium chloropalladite,** $CdPdCl_4$, in light brown needles, not changed in air; A. Welkow, **aluminium chloropalladite,** $PdCl_2.AlCl_3.10H_2O$, in dark brown deliquescent, rhombic prisms which lose 8 mols. of water at 130° to 140°, and decompose when the remainder of the water is driven off—the salt is soluble in water, alcohol, and ether; H. Gille, **thallous chloropalladite,** Tl_2PdCl_4; P. A. von Bonsdorff, **manganese chloropalladite,** $MnPdCl_4$, in black cubic crystals soluble in water and alcohol; and **nickel chloropalladite,** $NiPdCl_4$, in greenish-brown rhombohedra or hexagonal prisms permanent in dry air.

A. Gutbier and C. Fellner prepared some salts of the type $RCl.PdCl_2$, represented by **tripropylammonium trichloropalladite,** $\{(C_3H_7)_3NH\}PdCl_3$, in dark brown, pleochroic, monoclinic plates; **di-iso-butylammonium trichloropalladite,** $\{(C_4H_9)_2NH_2\}PdCl_3$, in dark brown, monoclinic plates; **tri-iso-butylammonium chloropalladite,** $\{(C_4H_9)_3NH\}PdCl_3$,

in brown, pleochroic, monoclinic plates ; **guanidinium trichloropalladite,** $\{NH : C(NH_2)_2.H\}PdCl_3$, in dark red crystals ; **amidoguanidinium trichloropalladite,** $\{NH : C.NH_2.NH.NH_3\}PdCl_3$, in reddish-brown crystals ; and **benzylethylammonium trichloropalladite,** $(C_6H_5.CH : NH.C_2H_5)PdCl_3$, in red, birefringent plates.

L. Wöhler and F. Martin observed that hydrated palladium sesquioxide is readily dissolved by hydrochloric acid, forming, presumably, **palladium trichloride,** $PdCl_3$, which is very unstable. If the sesquioxide is suspended in ether in the presence of rubidium chloride, at the temp. of solid carbon dioxide and ether, and hydrogen chloride is passed into the mixture, greyish-green crystals of **rubidium chloroperpalladite,** Rb_2PdCl_5, or $2RbCl.PdCl_3$, are formed ; and similarly with **cæsium chloroperpalladite,** Cs_2PdCl_5. Both salts decompose in contact with water to form the chloropalladites. If potassium chloride is employed in place of the rubidium salt, no **potassium chloroperpalladite,** K_2PdCl_5, is produced, but rather a mixture of $2KCl.PdCl_2$, and $4KCl.PdCl_2$. The formation of these characteristic double salts enables it to be shown that the trichloride is produced both when the dichloride is oxidized by means of chlorine and when the tetrachloride is reduced (by alcohol, for example). On the other hand, the trichloride cannot be obtained by reduction of double salts of the type $PdCl_4.2MCl$. There is therefore a difference in the behaviour of the free chlorides and those forming constituents of double salts in such a way that the free energy in the reaction $PdCl_2+PdCl_4 \rightarrow PdCl_3$ and $2K_2PdCl \rightarrow K_4PdCl_4+K_2PdCl_6$ diminishes in the directions indicated by the arrows. H. D. K. Drew and co-workers obtained **palladium diamminotrichloride,** $Pd(NH_3)_2Cl_3$, by chlorinating $Pd(NH_3)_2Cl_2$.

The chloride of quadrivalent palladium, **palladium tetrachloride,** or **palladic chloride,** $PdCl_4$, has not been isolated, but J. J. Berzelius obtained the salt in aq. soln., and also in combination with some metal chlorides. The aq. soln. is obtained by dissolving palladous chloride in conc. aqua regia with gentle heating, the dark brown soln. contains a mixture of palladous and palladic chlorides, and it gives a precipitate of potassium chloropalladate when treated with potassium chloride, whilst potassium chloropalladite remains in soln. A similar soln. can be obtained by dissolving hydrated palladium dioxide in conc. hydrochloric acid ; and H. Töpsöe obtained it by saturating a soln. of palladous chloride with chloride. J. J. Berzelius observed that the brown soln. of palladic chloride gradually gives off chlorine especially when it is diluted or evaporated, and it is thereby converted into a soln. of palladous chloride. H. B. Wellman studied the equilibrium of $PdCl_2$ and $PdCl_4$ in hydrochloric acid solutions. O. W. Gibbs observed that complex salts are formed with ammonium molybdate or sodium tungstate and palladium chloride.

H. D. K. Drew and co-workers obtained **palladic diamminochloride,** $Pd(NH_3)_2Cl_4$, as an orange powder, by the action of hydrochloric acid and hydrogen dioxide on palladous tetramminochloropalladite, or by chlorinating the dichlorodiammine suspended in carbon tetrachloride. The salt becomes black under water, and when the water is heated, there is formed the palladous dichlorodiammine. There was also prepared **palladic bispyridinochloride,** $(PdC_5H_5N)_2Cl_4$, obtained also by A. Rosenheim and T. A. Maass, as a reddish-orange powder ; and **palladic ethylenediaminochloride,** $PdenCl_4$, as a brown powder. If yellow palladous dichlorodiammine be chlorinated with cold hydrochloric acid and hydrogen dioxide, there is formed **palladium trichlorodiammine,** $[Pd(NH_3)_2Cl_3]_2$, in black shimmering needles, stable in air, but when heated with water palladous dichlorodiammine is produced.

A. Rosenheim and T. A. Maass prepared **palladic bispyridinochloride,** $[Pdpy_2]Cl_4$, by the action of chlorine on the corresponding palladous salt suspended in chloroform. The orange prisms give off chlorine in damp air ; when heated with potash lye, a brown precipitate of palladium hydroxide is obtained, and when the cold product is neutralized with hydrochloric acid, potassium chloropalladate formed. When shaken with an aq. soln. of iodine, palladous dichlorodipyridine is formed.

H. D. K. Drew and co-workers prepared **palladous tetramminochloropalladate,** $[Pd(NH_3)_4]PdCl_4$, by chlorinating the tetramminochloropalladite. It forms as a brownish-yellow powder, and when heated with water, it loses chlorine successively forming $[Pd(NH_3)_4]PdCl_4$, and $2[Pd(NH_3)_2Cl_2]$. They also prepared **palladous bisethylenediaminochloropalladate,** $[Pd\,en_2]PdCl_6$.

J. Thomsen gave the following as doubtful values for the heat of formation of **hydrochloropalladic acid,** H_2PdCl_6,(Pd,2Cl$_2$,2HCl,Aq.)=72·94 Cals.; (Pd(OH)$_4$,6HCl,Aq.)=21·950 Cals.; and (PdO$_2$,6HCl,Aq.)=52·38 Cals. J. J. Berzelius, and N. W. Fischer prepared **potassium chloropalladate,** K_2PdCl_6, or 2KCl.PdCl$_4$, by evaporating a soln. of potassium chloropalladite with aqua regia; H. Töpsöe, by saturating a soln. of palladous chloride with chlorine, and then adding a conc. soln. of potassium chloride, and well washing the crystalline precipitate with cold water; H. Croft, by saturating a hot, conc. soln. of the chloropalladite with chlorine; and G. Scagliarini and G. B. Berti-Ceroni, by warming the chloropalladite with potassium persulphate in the presence of hydrochloric acid, and cooling the soln. The structure of palladium salts was discussed by T. M. Lowry. Potassium chloropalladate, said J. J. Berzelius, forms vermilion-red, octahedral crystals belonging to the cubic system; when the crystals are large, the colour is brownish-red. H. Töpsöe found the sp. gr. to be 2·738. According to J. J. Berzelius, potassium chloropalladate fuses when heated, gives off chlorine, and passes into the chloropalladite. F. Puche observed that K_2PdCl_6 passes into K_2PdCl_4. J. Thomsen, and F. Puche gave for the heat of formation (Pd,2Cl$_2$,2KCl)=79·06 Cals.; and for the heat of soln., −15 Cals. R. Samuel and co-workers studied the absorption spectrum. H. B. Wellman measured the solubility of the chloropalladate in *N*-HCl, sat. with chlorine, at 25° and 740 mm. The solubility product $[K^{\cdot}]^2[PdCl_6'']$ is constant, and equal to $5{\cdot}97\times10^{-6}$ with molar concentrations. The oxidation equilibrium: $PdCl_4''+2Cl=PdCl_6''$ is established by passing chlorine through a soln. of the chloropalladite in *N*-HCl. The palladium is present as $PdCl_6''$ and $PdCl_4''$-ions, and not as hydrolyzed, or non-ionized acids. The reduction potential of $PdCl_4''+2Cl=PdCl_6''+2\epsilon$ at 25° is −1·288 volt.

V. Ipatéeff and V. G. Troneff studied the displacement of palladium from aq. soln. by hydrogen under press. J. J. Berzelius observed that the salt dissolves with difficulty in cold water forming a yellow soln. which consists mainly of chloropalladite and free chlorine mixed with some chloropalladate; when the salt is boiled with water, it gives off chlorine, and deposits some hydrated palladium dioxide whilst the liquid retains some hydrochloric acid; boiling for a longer time converts it completely into the chloropalladite. It dissolves in boiling water in a stoppered flask, a dark coloured soln. is obtained which, on cooling, deposits some chloropalladate, and the partially decolorized mother-liquid contains some chloropalladite and chlorine. The chloropalladate dissolves without decomposition in dil. hydrochloric acid, and is left unaltered when the liquid is evaporated; it is insoluble in water containing ammonium, potassium, or sodium chloride; it is decomposed by aq. ammonia with the evolution of nitrogen, and forms the chloropalladite; it is insoluble in alcohol; and when boiled with alcohol which has no action on it in the cold, it is decomposed with the evolution of ethereal vapours. C. Reichard observed that an arsenite is formed when the soln. is treated with potassium hydroarsenite.

A. Gutbier and A. Krell obtained **rubidium chloropalladate,** Rb_2PdCl_6, by passing chlorine into an aq. soln. of the chloropalladite. The red, microcrystalline precipitate is insoluble in cold water. They obtained **cæsium chloropalladate,** Cs_2PdCl_6, in a similar manner. The yellowish-brown, microscopic crystals are stable in air, nearly insoluble in cold water, lose chlorine when boiled with water, and are reduced by ammonia. The crystals were also examined by E. H. Ducloux. J. J. Berzelius prepared **ammonium chloropalladate,** $(NH_4)_2PdCl_6$, by mixing a soln. of palladium in aqua regia with ammonium chloride; and H. Töpsöe, by

adding ammonium chloride to a soln. of palladous chloride saturated with chlorine. The crystals are washed with ice-water saturated with ammonium chloride. The red, crystalline powder consists of octahedra analogous with those of the potassium salt. H. Töpsöe gave 2·418 for the sp. gr. S. F. Schemtschuschny found that a sat., 28·22 per cent. aq. ammonium chloride, at 25°, dissolves 0·26 per cent. of ammonium chloropalladate.

A. Gutbier and co-workers prepared **methylammonium chloropalladate**, $(CH_3NH_3)_2PdCl_6$; **dimethylammonium chloropalladate**, $\{(CH_3)_2NH_2\}_2PdCl_6$, in light red plates; **trimethylammonium chloropalladate**, $\{(CH_3)_3NH\}_2PdCl_6$, in dark red, crystalline powder; **tetramethylammonium chloropalladate**, $\{(CH_3)_4N\}_2PdCl_6$, in dark red needles; **ethylammonium chloropalladate**, $(C_2H_5.NH_3)_2PdCl_6$; **diethylammonium chloropalladate**, $\{(C_2H_5)_2NH_2\}_2PdCl_6$, in red needles; **triethylammonium chloropalladate**, $\{(C_2H_5)_3NH\}_2PdCl_6$, in light red crystals; **tetraethylammonium chloropalladate**, $\{(C_2H_5)_4N\}_2PdCl_6$, in bright red crystals; **iso-propylammonium chloropalladate**, $(C_3H_7NH_3)_2PdCl_6$, in bright red plates; **dipropylammonium chloropalladate**, $\{(C_3H_7)_2NH_2\}_2PdCl_6$, in purple-red plates; **tripropylammonium chloropalladate**, $\{(C_3H_7)_3NH\}_2PdCl_6$, in dirty red needles; **iso-butylammonium chloropalladate**, and **n-butylammonium chloropalladate**, $(C_4H_9.NH_3)_2PdCl_6$, in brownish-red plates; **di-iso-butylammonium chloropalladate**, $\{(C_4H_9)_2NH_2\}_2PdCl_6$, in reddish-brown plates; **tri-iso-butylammonium chloropalladate**, $\{(C_4H_9)_3NH\}_2PdCl_6$, in reddish-brown plates; **iso-amylammonium chloropalladate**, $(C_5H_{11}.NH_3)_2PdCl_6$, in purple red crystals; **di-iso-amylammonium chloropalladate**, $\{(C_5H_{11})_2NH_2\}_2PdCl_6$, in deep red crystals; **tri-iso-amylammonium chloropalladate**, $\{(C_5H_{11})_3NH\}_2PdCl_6$, in brownish-red crystals; **pyridinium chloropalladate**, $(C_5H_6N)_2PdCl_6$; **picolinium chloropalladate**, $(C_5H_4.CH_3.NH)_2PdCl_6$, in purple red crystals, in its α- and β-forms; **lutidinium chloropalladate**, $\{C_5H_3(CH_3)_2NH\}_2PdCl_6$, in brownish-red needles; **collidinium chloropalladate**, $\{(C_5H_2(CH_3)_3NH\}_2PdCl_6$, in red needles; and **iso-quinolinium chloropalladate**, $\{(C_9H_7.NH)\}_2PdCl_6$, in bright red needles.

R. Möhlan noted that the tertiary-cyclic bases unite with palladic chloride, forming compounds of the type: $PdCl_4.2R.HCl$, where R denotes pyridine, 2-phenyl-pyridine, quinoline, 2-methylquinoline, 8-phenylquinoline, and benzothiazole. Tertiary alkaloids also yield coloured compounds.

P. A. von Bonsdorff obtained **calcium chloropalladate**, and **barium chloropalladate** soluble in water and in alcohol. A. Welkow prepared **beryllium chloropalladate**, $BePdCl_6.8H_2O$, from a soln. of beryllium and palladic chlorides. The dark brown, hygroscopic crystals lose their water of crystallization at 150°. P. A. von Bonsdorff obtained **magnesium chloropalladate**, $MgPdCl_6.6H_2O$, by saturating a soln. of the chloropalladite with chlorine, and evaporating in an atm. of chlorine. The scarlet, rhombohedral crystals are deliquescent, and, according to H. Töpsöe, have a sp. gr. 2·12. P. A. von Bonsdorff similarly prepared **zinc chloropalladate**, $ZnPdCl_2.6H_2O$, in deep red, rhombohedral crystals which, according to H. Töpsöe, have a sp. gr. of 2·359. P. A. von Bonsdorff likewise obtained **cadmium chloropalladate**. P. A. von Bonsdorff, and H. Töpsöe also prepared **manganese chloropalladate**, $MnPdCl_6.6H_2O$, in scarlet, hygroscopic, rhombohedral crystals; and **nickel chloropalladate**, $NiPdCl_6.6H_2O$, in reddish-brown, hygroscopic, rhombohedral crystals of sp. gr. 2·353.

I. Bellucci and P. de Cesaris assumed that an aq. soln. of palladous chloride contained **dihydroxydichloropalladic acid**, $H_2Pd(OH)_2Cl_2$, because the addition of a silver salt precipitates not silver chloride, but rather **silver dihydroxydichloropalladate**, $Ag_2Pd(OH)_2Cl_2$. Likewise also, a lead salt precipitates a basic **lead dihydroxydichloropalladate**, $Pb[PdCl_2(OH)_2].Pb(OH)_2$; and a thallous salt, **thallous dihydroxydichloropalladate**, $Tl_2[PdCl_2(OH)_2]$. All three salts appear as amorphous precipitates. The silver salt is slowly hydrolyzed by hot water, and the other salts more rapidly.

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§ 10. Palladium Bromides

According to J. Nicklès,[1] palladium is only attacked a little by a soln. of bromine in aq. ether. P. A. von Bonsdorff obtained **palladous bromide,** $PdBr_2$, by the action of a mixture of hydrobromic and nitric acids on the metal, and removing the nitrous acids by boiling and evaporation with an excess of hydrobromic acid. G. Beck found the sp. gr. to be 5·173 at 16°, and the mol. vol. 51·5. A. Joannis gave for the heat of formation $(Pd,Br_{liquid})=24{\cdot}88$ Cals. The brown, amorphous mass is insoluble in water and in alcohol, but it is decomposed by water; it is soluble in dil. hydrobromic acid. Ammonia converts it into palladous dibromodiammine. W. Strecker and M. F. Schurigin found that phosphorus tribromide furnishes **palladous phosphorus pentabromide,** $PdBr_2.PBr_3$, as in the case of the corresponding chloride.

H. Fehling, and H. Müller obtained **palladous dibromodiammine,** $[Pd(NH_3)_2Br_2]$, by pouring palladous bromide into an excess of aq. ammonia, when a brown precipitate of the tetramminochloropalladite is formed. This dissolves in aq. ammonia, and when the soln. is filtered into hydrobromic acid in excess, yellow, octahedral crystals of the dichlorodiammine are formed. A. Gutbier and co-workers prepared the dibromodiammine as follows:

Purified palladium was dissolved in a mixture of hydrobromic and nitric acids. The latter acid was expelled by repeated evaporation with hydrobromic acid, the residue dissolved in a small quantity of hydrobromic acid, and filtered into excess of ammonium hydroxide. A brown precipitate of the salt $Pd(NH_3)_4Br_2,PdBr_2$ was produced, but on prolonged digestion with ammonium hydroxide it dissolved, with the formation of the dibromoammine $Pd(NH_3)_2Br_2$. The soln. was filtered into excess of hydrobromic acid,

whereby the dibromoammine was obtained as a yellow, finely crystalline precipitate. The precipitate was washed free from ammonium bromide, again dissolved in ammonium hydroxide, and precipitated with hydrobromic acid, the process being repeated three times. The pure bromide thus obtained was dried at 105° to 110° to constant weight.

G. Beck gave 3·372 for the sp. gr. at 17° ; 89·2 for the mol. vol. ; and 145 Cals. for the heat of formation. According to H. Müller, the salt is insoluble in cold water, but soluble in hot water. The prolonged action of boiling water decomposes the salt with the loss of ammonia and the separation of brown flecks. Hydrochloric acid converts it slowly with the chloro-compound ; it does not dissolve in sulphurous acid, nor in a soln. of potassium hydroxide.

A. Gutbier and co-workers prepared **palladous dibromobis-iso-propylamine,** $[Pd(C_3H_7NH_2)_2Br_2]$, in yellow crystals ; **palladous dibromobisdipropylamine,** $[Pd\{(C_3H_7)_2NH\}_2Br_2]$, in yellow needles ; **palladous dibromobis-n-butylamine,** $[Pd(C_4H_9NH_2)_2Br_2]$, as a yellow, crystalline powder ; **palladous dibromobis-iso-butylamine,** $[Pd\{(C_4H_9)_2NH\}_2Br_2]$, in dark yellow crystals ; **palladous dibromobis-iso-amylamine,** $[Pd(C_5H_{11}.NH_2)_2Br_2]$, in yellow crystals ; **palladous dibromobisdi-iso-amylamine,** $[Pd\{(C_5H_{11})_2NH\}_2Br_2]$, in yellow plates ; **palladous dibromobisphenylamine,** $(Pd_2(C_6H_5NH_2)_2$; **palladous dibromobistolylamine,** $PdBr_2(C_7H_7NH_2)_2$; **palladous dibromobismethylphenylamine,** $Pd\{(CH_3)(C_6H_5)NH\}_2Br_2$; **palladous dibromobisethylphenylamine,** $Pd\{(C_2H_5)(C_6H_5)NH\}_2Br_2$; **palladous dibromobisxylylamine,** $PdBr_2\{C_6H_3(CH_3)_2NH_2\}_2$; **palladous dibromobis-p-anisidylamine,** $PdBr_2\{C_6H_4(OCH_3)NH_2\}_2$; **palladous dibromobis-α-naphthylamine,** $PdBr_2(C_{10}H_7.NH_2)_2$; **palladous dibromobis-β-naphthylamine ; palladous dibromobisbenzidylamine,** $PdBr_2(C_{12}H_8(NH_2)_2$; **palladous dibromo-o-phenylenediamine,** $PdBr_2.C_6H_4(NH_2)_2$; **palladous dibromobis-1.2.4-xylidine,** $[Pd\{C_6H_3(CH_3)_2NH_2\}_2Br_2]$, in golden yellow needles ; **palladous dibromobis-1.3.4-xylidine,** in dark golden-yellow needles ; **palladous dibromobis-1.4.5-xylidine,** in dark yellow needles ; **palladous dibromo-1.3.4-toluylenediamine,** $[Pd\{C_6H_3(CH_3)(NH_2)_2\}Br_2$, in pale brown plates ; **palladous dibromobis-β-picoline,** $[Pd\{C_5H_4(CH_3)N\}_2Br_2]$, in yellow plates ; **palladous dibromobislutidine,** $[Pd\{C_5H_3(CH_3)_2N\}_2Br_2]$, in dark yellow plates ; **palladous dibromobiscollidine,** $[Pd\{C_5H_3(CH_3)_2N\}_2Br_2]$, in dark golden-yellow plates ; W. L. Hardin, and A. Gutbier and co-workers, **palladous dibromobispiperidine,** $[Pd(C_5H_{10}NH)_2Br_2]$, in yellow crystals ; and **palladous dibromobis-iso-quinoline,** $[Pd(C_9H_7N)_2Br_2]$, in brownish plates. A. Rosenheim and T. A. Maass obtained the quinoline salt in reddish-brown leaflets ; A. Gutbier and C. Fellner, **palladous dibromobispyridine,** $[Pdpy_2Br_2]$, as a yellow, crystalline powder ; and A. Rosenheim and T. A. Maass, **palladous dibromobisbenzylamine,** $[Pd(C_6H_5.CH_2.NH_2)_2Br_2]$, in golden-yellow leaflets ; **palladous dibromobisbenzylbromoamine,** $Pd\{NH_3(CH_2.C_6H_5)Br\}_2Br_2$; **palladous dibromobisdibenzylbromoamine,** $Pd\{NH_2(CH_2.C_6H_5)_2Br\}_2Br_2$; **palladous dibromobisbenzylamine,** $Pd(NH_2.CH_2.C_6H_5)_2Br_2$; **palladous dibromobispyridine,** $Pd(C_5H_5N)_2Br_2$; **palladous dibromobis-2-methylpyridine,** $Pd\{C_5H_4(CH_3)N\}_2Br_2$; **palladous dibromobis-α-picoline,** $Pd\{C_5H_4N(CH_3)\}_2Br_2$; and **palladous dibromobisquinoline,** $Pd(C_9H_7N)_2Br_2$. E. C. Fritzmann, and L. Tschugaeff and C. Iwanoff described **palladous dibromobisdiethylsulphine,** $[Pd\{(C_2H_5)_2S\}_2Cl_2$; **palladous dibromobismethylethylsulphine,** $[Pd(CH_2SC_2H_5)_2Br_2]$; **palladous dibromoethylenebisdiethylsulphine,** $[Pd\{S(C_2H_5).CH_2.CH_2.S(C_2H_5)\}Br_2]$; **palladous dibromobismethylselenine,** $PdBr_2.2(CH_3)_2Se$; **palladous dibromobisethylselenine,** $PdBr_2.2(C_2H_5)_2Se$; **palladous dibromobispropylselenine,** $PdBr_2.2(C_3H_7)_2Se$; **palladous dibromobisbutylselenine,** $PdBr_2.2(C_5H_9)_2Se$; **palladous dibromobispentylselenine,** $PdBr_2.2(C_5H_{11})_2Se$; **palladous dibromobisphenylselenine,** $PdBr_2.2(C_6H_5)_2Se$; and **palladous dibromodiethyltrimethyleneselenide,** $PdBr_2.(C_2H_5)Se(CH_2)_3Se(C_2H_5)$.

H. Müller prepared **palladous tetramminobromide,** $[Pd(NH_3)_4]Br_2$, by dissolving palladous bromide, or dibromodiammine in an excess of aq. ammonia. It crystallizes in almost colourless rhombic prisms, which are stable in air, and soluble in water. G. Beck found the sp. gr. to be 2·320 at 16° ; the mol. vol. 152·6 ; and the heat of formation 528 Cals. H. Fehling, and H. Müller prepared **palladous tetramminobromopalladite,** $[Pd(NH_3)_4]PdBr_4$, as a red precipitate, insoluble in water, by adding palladous bromide to the tetramminobromide, and by adding an excess of ammonia to a soln. of palladous bromide. For the process of A. Gutbier and co-workers, *vide supra.* P. A. von Bonsdorff prepared the complex $[Pd(NH_3)_2Br_2]_4[Pd(NH_3)_4]Br_2$, which has yellow, tetragonal crystals with $a : c = 1 : 1·1487$.

A. Gutbier and C. Fellner prepared **palladous quater-iso-propylaminobromopalladite,** $[Pd(C_3H_7.NH_2)_4]PdBr_4$; **palladous quater-n-butylaminobromopalladite,** $[Pd(C_4H_9.NH_2)_4]PdBr_4$; and **palladous quater-iso-amylaminobromopalladite,** $[Pd(C_5H_{11}.NH_2)_4]PdBr_4$. A. Gutbier and M. Woernle obtained **palladous bisethylenediaminobromide,** $[Pd\,en_2]Br_4$, in dark

yellow crystals; and similarly with **palladous bispropylenediaminebromide**, $[Pdpn_2]Br_2$; and **palladous bisdibenzylaminodibromide**, $Pd\{NH(CH_2.C_6H_5)_2\}_2Br_2$.

P. A. von Bonsdorff, and E. F. Smith and D. L. Wallace prepared **potassium bromopalladite**, K_2PdBr_4, by evaporating a mixed soln. of potassium and palladous bromides in water containing hydrobromic acid. The salt appears in reddish-brown needles which are unchanged after exposure to air. A. Joannis gave for the heat of formation for the solid salt, $(PdBr_2,2KBrAq.)=K_2PdBr_4(solid)+15{\cdot}32$ Cals., and for K_2PdBr_4(soln.), 2·84 Cals. When the soln. is treated with bromine at 70°, the bromopalladate is not formed, but the *dihydrate*, $K_2PdBr_4.2H_2O$, crystallizes from the soln. in dark brown needles, which lose their lustre on exposure to air, and form a reddish-brown powder. W. Jander studied the system K_2PdCl_6–K_2PdBr_4. A. Gutbier and A. Krell found that **rubidium bromopalladite**, $RbPdBr_4$, is precipitated in reddish-brown, acicular crystals on mixing conc. soln. of rubidium and palladous bromides. The salt is recrystallized from its soln. in dil. hydrobromic acid. The salt is soluble in water. Similarly with **cæsium bromopalladite**, Cs_2PdBr_4, which furnishes reddish-brown needles, which are very soluble in water. The corresponding **ammonium bromopalladite**, $(NH_4)_2PdBr_4$, was prepared in an analogous manner by A. Gutbier and A. Krell, and E. F. Smith and D. L. Wallace. The olive-brown, rhombic crystals are stable on exposure to air. They are soluble in water. G. Scagliarini and G. B. Berti-Ceroni found that when the acidified soln. of potassium or ammonium bromopalladite is treated with a persulphate, the corresponding bromopalladate is precipitated.

A. Gutbier and co-workers prepared **tetramethylammonium bromopalladite**, $\{(CH_3)_4N\}_2PdBr_4$, as a reddish-brown, crystalline powder; **iso-propylammonium bromopalladite**, $(C_3H_7NH_3)_2PdBr_4$, in dark reddish-brown plates; **n-butylammonium bromopalladite**, $(C_4H_9NH_3)_2PdBr_4$, in reddish-brown plates; **di-iso-butylammonium bromopalladite**, $\{(C_4H_9)_2NH_2\}_2PdBr_4$, in reddish-brown plates; **tri-iso-butylammonium bromopalladite**, $\{(C_3H_5)_3NH\}_2PdBr_4$, in bronze plates; **allylammonium bromopalladite**, $(C_3H_5.NH_3)_2PdBr_4$, in dark brown plates; **iso-amylammonium bromopalladite**, $(C_5H_{11}NH_3)_2PdBr_4$, in dark reddish-brown plates; **di-iso-amylammonium bromopalladite**, $\{(C_5H_{11})_2NH_2\}_2PdBr_4$, in brown plates; **tri-iso-amylammonium bromopalladite**, $\{(C_5H_{11})_3NH\}_2PdBr_4$, in dark reddish-brown plates; **guanidinium bromopalladate**, $\{C.NH(NH_2)_2H\}_2PdBr_4$, in dark red needles; **anilinium bromopalladite**, $(C_6H_5NH_3)_2PdBr_2$; **bromoanilinium bromopalladite**, $(C_6H_4Br.NH_2)_2PdBr_4$, in dark red crystals; **m-bromoanilinium bromopalladite**, in red needles; **methylanilinium bromopalladite**, $\{(C_6H_5)(CH_3)NH_2\}_2PdBr_4$; **ethylanilinium bromopalladite**, $\{(C_6H_5)(C_2H_5)NH_2\}_2PdBr_4$; **diethylanilinium bromopalladite**, $\{(C_6H_5)(C_2H_5)_2NH\}_2PdBr_4$; **p-anisidinium bromopalladite**, $\{C_6H_4(OCH_3).NH_3\}_2PdBr_4$; **naphthylamine bromopalladite**, $(C_{10}H_7.NH_3)_2PdBr_4$—in its α- and β-forms; **benzidinium bromopalladite**, $C_{12}H_8(NH_3)_2PdBr_4$; ***m*-phenylenediamine bromopalladite**, $C_6H_4(NH_3)_2.PdBr_4$; **toluidinium bromopalladite**, $(C_7H_7NH_3)_2$—in its *o*- and *p*-forms; **dimethyl-o-toluidinium bromopalladite**, $\{C_6H_4.CH_3.NH.(CH_3)_2\}_2PdBr_4$, in dark carmine-red crystals; **xylidinium-1.2.4-bromopalladite**, $\{C_6H_3(CH_3)_2NH_3\}_2PdBr_4$, in reddish-brown plates; **xylidinium-1.3.4-bromopalladite**, in brownish-red plates; **xylidinium-1.4.5-bromopalladite**, in dark reddish-brown plates; **pseudocumidinium bromopalladite**, $\{C_6H_2(CH_3)_3NH_3\}_2PdBr_4$, in dark reddish-brown plates; **β-picolinium bromopalladite**, $(C_5H_4.CH_3.NH)_2PdBr_4$, in dark red crystals; **lutidinium bromopalladite**, $\{C_5H_3(CH_3)_2NH\}_2PdBr_4$, in dark brownish-red crystals; **piperidinium bromopalladite**, $(C_5H_{10}NH_2)_2PdBr_4$, in dark red crystals; and **iso-quinolinium bromopalladite**, $(C_9H_7NH)_2PdBr_4$, in reddish-brown crystals.

E. F. Smith and D. L. Wallace prepared **sodium bromopalladite**, $2Na_2PdBr_4.9H_2O$, by concentrating a mixed soln. of the component bromides over sulphuric acid in an evacuated desiccator. The dark red tablets are very deliquescent. E. F. Smith and D. L. Wallace, and A. Gutbier and A. Krell prepared **strontium bromopalladite**, $SrPdBr_4.6H_2O$, in black prisms, stable in air; P. A. von Bonsdorff, **barium bromopalladite**, $BaPdBr_4$, in dark brown prisms, stable in air; and **zinc bromopalladite**, $ZnPdBr_4$, in dark brown crystals, soluble in water. E. F. Smith and D. L. Wallace were unable to prepare the zinc salt, and likewise **cadmium bromopalladite**. E. F. Smith and D. L. Wallace prepared **manganese bromopalladite**, $MnPdBr_4.7H_2O$, in black crystals very soluble in water.

A. Gutbier and C. Fellner prepared some salts of the type $RBr.PdBr_2$, for example: **tetraethylammonium tribromopalladite**, $\{(C_2H_5)_4N\}PdBr_3$, in dark brown crystals; **tripropylammonium tribromopalladite**, $\{(C_3H_7)_3NH\}PdBr_3$, in dark brown crystals; **collidinium bromopalladite**, $\{C_5H_2(CH_3)_3NH\}PdBr_3$, in dark brown crystals; and **tribenzylammonium bromopalladite**, $\{C_6H_5.CH_2)_3NH\}PdBr_3$, in dark reddish-brown crystals.

Complex salts of **palladic bromide,** or **palladium tetrabromide,** $PdBr_4$, have been prepared, but not the parent salt. A. Gutbier and A. Krell prepared **potassium bromopalladate,** K_2PdBr_6, by passing a current of bromine vapour through a soln. of the bromopalladite, and G. Scagliarini and G. B. Berti-Ceroni, by oxidizing a soln. of the bromopalladite with potassium persulphate in the presence of hydrobromic acid. The black, octahedral crystals are sparingly soluble in cold water to form a reddish-brown soln., but are decomposed by boiling water; and by sulphuric acid with the evolution of bromine; and by ammonia, with the evolution of nitrogen. A. Gutbier and A. Krell prepared **rubidium bromopalladate,** Pb_2PdBr_6, as insoluble, black, octahedral crystals; and **cæsium bromopalladate,** Cs_2PdBr_6, also as black octahedral crystals, by the process used for the corresponding chloro-salt. P. Stoll found that the X-radiograms of the rubidium salt correspond with a face-centred cubic lattice similar to that of potassium chloroplatinate; and that the parameter $a=10{\cdot}02$ A., and the distance apart of palladium and bromine atoms is 2·52 A. L. Pauling and M. L. Huggins discussed the subject. By a similar process **ammonium bromopalladate,** $(NH_4)_2PdBr_6$, was obtained in black, octahedral crystals which are stable in air; soluble in cold water to form a reddish-brown soln.; and when heated in a dry tube, they first give off bromine, then ammonium bromide vapour, and there remains spongy palladium. Hot water, sulphuric acid, and aq. ammonia decompose the salt as in the case of the potassium salt.

A. Gutbier and M. Woernle, and A. Gutbier and C. Fellner prepared **methylammonium bromopalladate,** $(CH_3.NH_3)_2PdBr_6$; **dimethylammonium bromopalladate,** $\{(CH_3)_2NH_2\}_2PdBr_6$, in dark green needles; **trimethylammonium bromopalladate,** $\{(CH_3)_3NH\}_2PdBr_6$, in dark green crystals; **tetramethylammonium bromopalladate,** $\{(CH_3)_4N\}_2PdBr_6$, in dark green crystals; **ethylammonium bromopalladate,** $(C_2H_5.NH_3)_2PdBr_6$; **diethylammonium bromopalladate,** $\{(C_2H_5)_2NH_2\}_2PdBr_6$, in bluish-green needles; **triethylammonium bromopalladate,** $\{(C_2H_5)_3NH\}_2PdBr_6$, in dark green crystals; **tetraethylammonium palladate,** $\{(C_2H_5)_4N\}_2PdBr_6$, in greenish-black needles; **iso-propylammonium bromopalladate,** $(C_3H_7.NH_3)_2PdBr_6$, in dark greenish-blue needles; **dipropylammonium bromopalladate,** $\{(C_3H_7)_2NH_2\}_2PdBr_6$, in dark green plates; **tripropylammonium bromopalladate,** $\{(C_3H_7)_3NH\}_2PdBr_6$, in greenish-black needles; **n-butylammonium bromopalladate,** $(C_4H_9NH_3)_2PdBr_6$, in black needles; **di-iso-butylammonium bromopalladate,** $\{(C_4H_9)_2NH_2\}_2PdBr_6$, in dark green crystals; **tri-iso-butylammonium bromopalladate,** $\{(C_4H_9)_3NH\}_2PdBr_6$, in greenish-black needles; **iso-amylammonium bromopalladate,** $(C_5H_{11}NH_3)_2PdBr_6$, in dark green plates; **di-iso-amylammonium bromopalladate,** $\{(C_5H_{11})_2NH_2\}_2PdBr_6$, in dark bluish-green crystals; **tri-iso-amylammonium bromopalladate,** $\{(C_5H_{11})_3NH\}_2PdBr_6$, in dark green needles; **pyridinium bromopalladate,** $(C_5H_6N)_2PdBr_6$; **α-picolinium bromopalladate,** $(C_5H_4.CH_3.NH)_2PdBr_6$, in bluish-black crystals; **β-picolinium bromopalladate,** in brownish-black plates; **lutidinium bromopalladate,** $\{C_5H_3(CH_3)_2NH\}_2PdBr_6$, in black needles; **collidinium bromopalladate,** $\{C_5H_2(CH_3)_3NH\}_2PdBr_6$, in almost black crystals; **quinolinium bromopalladate,** $(C_9H_7.NH)_2PdBr_6$, in brownish-black needles; and **iso-quinolinium bromopalladate,** in brownish- or greenish-black needles.

A. Gutbier and C. Fellner prepared **o-bromoanilinium chloropalladite,** $(C_6H_4Br.NH_3)_2PdCl_4$, in yellowish-brown crystals; **p-bromoanilinium chloropalladite,** $(C_6H_4Br.NH_3)_2PdCl_4$, in orange-brown needles; and **m-chloroanilinium bromopalladite,** $(C_6H_4Cl.NH_3)_2PdBr_4$, in copper-red plates.

A. Rosenheim and T. A. Maass prepared **palladic bispyridinochlorobromide,** $[Pdpy_2]Cl_2Br_2$, by shaking bromine with palladous dichlorobispyridine suspended in chloroform. The orange-red powder is less stable than the tetrachloride; and it furnishes the chloropalladate when boiled with potash lye.

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§ 11. Palladium Iodides

J. L. Lassaigne [1] observed that when palladium is exposed to the vapours of iodine, it acquires a brown tarnish; union is imperfect when finely-divided palladium and iodine are heated together, and also when palladium is boiled with iodine water, or with a mixture of hydriodic and nitric acids. J. L. Lassaigne, and A. Gutbier and A. Krell recommended preparing **palladous iodide, or palladium diiodide,** PdI_2, by the addition of potassium iodide to a soln. of a palladous salt in slight excess, washing the precipitate with boiling water, and drying it for 24 hrs. in vacuo. When dried in air, the *monohydrate*, $PdI_2.H_2O$, is formed. The dissociation press. was found by F. Isambert to be 760 mm. at 235°. G. Beck gave 6·003 for the sp. gr. at 18°, and 60·0 for the mol. vol. A. Joannis gave for the heat of formation $(Pd,I_2)=13{\cdot}4$ Cals. A. Eucken and A. Büchner studied the dielectric constant. When the diiodide is heated between 300° and 360°, it gives off the vapour of iodine, but to remove the last traces of iodine, the residue must be heated to redness in hydrogen. The diiodide is insoluble in water, alcohol, and ether; it is slightly soluble in hydriodic acid; easily soluble in a soln. of potassium iodide; it forms hydrated palladous oxide when heated with potash lye; and aq. ammonia converts it into the diiododiammine. According to H. Müller, if the conc. soln. of palladous iodide in aq. ammonia be allowed to stand in a warm place for some time, it deposits dark violet octahedra of unknown composition. R. Kersting added that the salt is soluble in aq. soln. of chlorine, bromine, and iodine; insoluble in hydrochloric acid, and in a soln. of potassium bromide except in the presence of a free mineral acid; it is soluble in sulphurous acid; insoluble in dil. sulphuric acid; soluble in ammonia with evolution of heat and decomposition; it is slightly soluble in hot, conc. nitric acid, but insoluble in dil. nitric acid; insoluble in dil. phosphoric acid; insoluble in acetic acid; soluble in an aq. soln. of cyanogen, in hydrocyanic acid, and in soln. of alkali cyanides; insoluble in soln. of sugar, starch, uric acid, alcohol, ether; insoluble in oil of lemons; somewhat soluble in urine; insoluble in soln. of potassium, sodium, or ammonium chlorides, sulphates, phosphates, nitrates, or acetates; and insoluble in soln. of cupric or zinc chloride, and in lead acetate. A. Naumann observed that the iodide is soluble in methyl acetate.

According to J. L. Lassaigne, the colourless soln. of palladous iodide in aq. ammonia deposits orange-yellow crystals of **palladous diamminodiiodide,** $[Pd(NH_3)_2I_2]$, when exposed to air; H. Fehling obtained it by adding hydrochloric

acid, or any other acid, to the pale yellow soln. of palladous iodide in aq. ammonia. The reddish-yellow powder which is deposited should be rapidly washed, and dried by press. between bibulous paper, and dried over warm sand. G. Beck gave 200 Cals. for the heat of formation. H. Fehling observed that the dry salt is permanent in air, but when moist, it quickly passes with the red salt; this conversion occurs during the washing, or when it is dried in vacuo, or by heat—unless previously pressed in filter-paper—and the change is completed in a few days. The yellow compound passes into the red salt by prolonged boiling with water. Boiling nitric acid dissolves the red salt and converts it into palladous nitrate.

According to F. G. Mann and co-workers, if the yellow powder is treated with cold acetone, it changes in a few seconds into reddish-blue, sparingly-soluble, octahedral crystals; and a similar conversion occurs when the yellow powder is treated with alcohol. The change in aqueous soln. at room temp. may take hours or days. The colour of the octahedra depends on their physical condition, since, when powdered, they are deep brick-red, showing that the blue surface reflexion makes well-formed crystals appear steel-blue. Both forms of the diiodide dissolve in excess of ammonia, forming palladous tetramminodiiodide, but if the soln. is exposed to air, the tetrammine decomposes, forming the diiododiammine in red, rhombic crystals, without the blue sheen, and they have the same crystalline X-radiograms as the yellow powder. After a few hours, the red crystals pass slowly into the reddish-blue form. If freshly-prepared palladous dichlorodiammine, dried without heating, be shaken with a conc. soln. of potassium iodide, the yellow form of the diiodide is first produced, and on standing it changes into reddish-blue octahedra; whereas with an aged sample of the dichlorodiammine, the change is much slower, and the intermediate yellow form may not appear. The X-radiograms of the reddish-blue form indicate that the iodine atoms, and the ammonia molecules occur in irregular positions along the *c*-axis, between consecutive molecular layers of the crystals. The effect is due to the repeated polysynthetic twinning of the crystals. The effect is observed, but more faintly, with the red crystals of the dichlorodiammine. According to H. Müller, the yellow and the red crystals are not two different forms of the diiododiammine.

A. Gutbier and C. Fellner prepared **palladous diiodobis-iso-propylamine,** $[Pd(C_3H_7NH_2)_2I_2]$, in brownish-yellow plates; **palladous diiodobis-n-butylamine,** $[Pd(C_4H_9NH_2)_2I_2]$, as a brownish-yellow, crystalline powder; **palladous diiodobis-iso-amylamine,** $[PdC_5H_{11}NH_2)_2I_2]$, in brownish-yellow plates; **palladous diiodobispyridine,** $[Pdpy_2I_2]$, as a dark yellow, crystalline powder; **palladous diiodo-α-picoline,** $[Pd(C_5H_4.CH_3.N)_2I_2]$, as a greyish-yellow, crystalline powder; **palladous diiodo-β-picoline,** in brownish-yellow crystals; **palladous diiodolutidine,** $[Pd\{C_5H_3(CH_3)_2N\}_2I_2]$, in dark brownish-yellow plates; **palladous diiodocollidine** $[Pd\{C_5H_2(CH_3)_3N\}_2I_2]$, in dark brownish-yellow plates; and **palladous diiodopiperidine,** $[Pd(C_5H_{10}NH)_2I_2]$, as a grey, microcrystalline powder; J. Thomsen gave $(Pd,I_2,H_2O)=18{\cdot}18$ Cals. for the heat of formation. F. G. Mann prepared **palladous bistriaminopropanoiodide,** $[Pd\{NH_2.CH_2.CH(NH_2).CH_2.NH_2\}_2]I_2$. F. G. Mann and W. J. Pope prepared **palladous diiodo-ββ′β″-triaminotriethylamine,** $[PdN(C_2H_4.NH_2)_3I_2]$. E. C. Fritzmann, L. Tschugaeff and C. Iwanoff, C. W. Blomstrand, and K. A. Hofmann and W. O. Rabe described **palladous diiodobis-diethylsulphine,** $[Pd\{(C_2H_5)_2S\}_2I_2$; **palladous diiodobismethylethylsulphine,** $[Pd(CH_2SC_2H_5)_2I_2]$; **palladous diiodo-ethylenebisdiethylsulphine,** $[Pd\{S(C_2H_5).CH_2.CH_2\}.S(C_2H_5)I_2]$; **palladous diiodobismethylselenine,** $PdI_2.2(CH_3)_2Se$; **palladous diiodobisethylselenine,** $PdI_2.2(C_2H_5)_2Se$; **palladous diiodobispropylselenine,** $PdI_2.2(C_3H_7)_2Se$; **palladous diiodobisbutylselenine,** $PdI_2.2(C_4H_9)_2Se$; and **palladous diiodobispentylselenine,** $PdI_2.2(C_5H_{11})_2Se$.

H. Fehling prepared **palladous tetramminoiodide,** $[Pd(NH_3)_4]I_2$, by evaporating in an atm. of ammonia, a soln. of the diiododiammine or palladous iodide in conc. ammonia; and by F. Isambert, by passing ammonia over dry palladous iodide. The colourless crystals lose ammonia when exposed to air, and become yellow; and in vacuo, the diiododiammine is first formed, and then palladous iodide. F. Isambert found the dissociation press. to be 760 mm. at 100°; and the heat of formation is $[Pd(NH_3)_2I_2]+2NH_3=[Pd(NH_3)_4]I_2+25{\cdot}76$ Cals. The red diiododiammine is

considered to be **palladous tetramminoiodopalladite,** $[Pd(NH_3)_4]PdI_2$—*vide supra.* W. A. Burdakoff obtained a complex with $[Pt(NH_3)_2Br_2]$.

A. Gutbier and M. Woernle prepared **palladous bisethylenediaminoiodide,** $[Pden_2]I_2$, in brownish-yellow crystals; and similarly with **palladous bispropylenediaminoiodide,** $[Pdpn_2]I_2$.

J. L. Lassaigne reported **potassium iodopalladite,** K_2PdI_4, in greyish-black, deliquescent cubes, to be formed by evaporating the wine-red soln. of palladous iodide in an aq. soln. of potassium iodide. A. Rosenheim and H. Itzig obtained **potassium diiododinitritopalladite,** $K_2PdI_2(NO_2)_2$, in purple, prismatic crystals.

A. Rosenheim and T. A. Maass obtained **palladic bispyridinodiiododichloride,** $[Pdpy_2]I_2Cl_2$, in brown needles which are stable in dry air, and decomposed by boiling potash lye. Carbon disulphide extracts the two atoms of iodine.

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§ 12. The Palladium Sulphides and Sulphates

According to J. J. Berzelius,[1] palladium when heated unites with sulphur with incandescence. R. Schneider reported **palladium hemisulphide,** Pd_2S, or **palladium subsulphide** to be formed by melting an intimate mixture of 1 part of palladous sulphide with 6 parts of ammonium chloride, 12 of sodium hydroxide, and 12 of sulphur, and washing the product with water. F. Rössler obtained it by heating palladous dichlorodiammine with 25 per cent. of its weight of sulphur, under a layer of borax at about 1064°. R. Schneider, and F. Rössler observed that the grey regulus is hard and brittle; it has a crystalline fracture, and a sp. gr. of 7·303 at 15°; it melts at a red-heat; and when heated at a high temp., or in hydrogen, it slowly loses sulphur; it is not attacked by the simple acids at ordinary temp.; boiling nitric acid has a slight action; and it is soluble in aqua regia. F. Weibke and J. Laar showed that the only stable lower sulphide at room temp. is palladium tetritasulphide, Pd_4S. The equilibrium diagram is illustrated in Fig. 35. The β-solid soln. stable at high temperatures undergoes peritectic decomposition at 554° into Pd_4S+PdS. With 69·5 at. per cent. of Pd, two liquid phases occur. Sulphur is not soluble in solid palladium.

L. N. Vauquelin prepared **palladium monosulphide,** or **palladous sulphide,** PdS, by heating palladous dichlorodiammine with sulphur; and E. F. Smith and H. F. Keller, by passing hydrogen sulphide over the dichlorodiammine at 70° to 80°—here the mass becomes black and at higher temp. ammonium chloride volatilizes leaving a residue of the sulphide. The palladous sulphide so obtained

is a bluish-white, hard regulus with a crystalline fracture which, according to L. N. Vauquelin, is molten at 960°. F. Weibke and J. Laar gave 940° for the m.p. H. G. Krall, and L. Wöhler and co-workers observed that palladium disulphide at 600° passes into the monosulphide. F. A. Bannister said that the tetragonal crystals have a space-lattice with a=6·37 A., and c=6·87 A., and a calculated sp. gr. of 6·87. Palladous sulphide was found by J. J. Berzelius, and L. N. Vauquelin to be slowly converted into a basic sulphate when it is heated in air, and at a higher temp., palladium is formed. The sulphide forms sulphur chloride and palladous chloride when it is heated in chlorine. The sulphide is insoluble in mineral acids, but soluble in aqua regia. L. R. von Fellenberg, J. J. Berzelius, and P. Petrenko-Kritschenko obtained another form of this sulphide as a precipitate on passing hydrogen sulphide through a soln. of palladous chloride, washing the precipitate quickly with boiling water, and drying it over sulphuric acid. The dark brown product is insoluble in ammonium sulphide, and in hydrochloric acid, but it is soluble in nitric

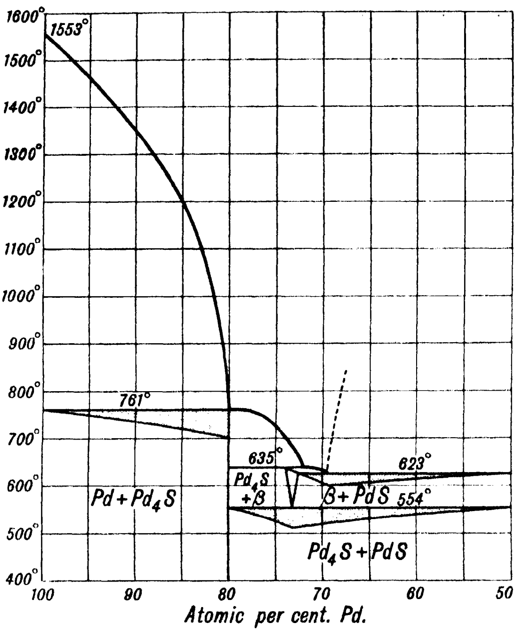

FIG. 35.—Equilibrium Diagram of the System Pd–PdS.

acid, and aqua regia, and, according to A. Béchamp, it is slowly soluble in a soln. of potassium cyanide. A. Mailfert said that the prolonged action of ozone converts the sulphide into a peroxide and sulphuric acid. K. A. Hofmann and F. Höchtlen, and F. Höchtlen prepared **ammonium palladium polysulphide,** $(NH_4)_2PdS_{11}.\frac{1}{2}H_2O$, by the action of ammonium polysulphide on a soln. of palladous chloride.

H. H. Croft said **palladous sulphodiammine,** $Pd(NH_3)_2S$, is one of the first products of the action of hydrogen sulphide on the dichlorodiammine, and that it appears as an orange precipitate which is rapidly converted into palladous sulphide. V. N. Ivanoff prepared **palladium dithiocarbamidosulphide,** $Pd_3S_2(CSNH_2)_2$.

R. Schneider prepared a **potassium sulphopalladite,** $K_2Pd_3S_4$, by heating to redness palladous sulphide with 12 times its weight of a mixture of equal parts of sulphur and potassium hydroxide, and leaching the cold product with water. The steel-blue, hexagonal crystals are stable in air, they are insoluble in water, and they are decomposed by hydrochloric acid. R. Schneider obtained **silver sulphopalladite,** $Ag_2Pd_3A_4$, by the action of a soln. of silver nitrate on potassium sulphopalladite, and washing the product with dil. nitric acid. The grey, hexagonal plates are insoluble in water ; they are attacked a little by aqua regia ; and when heated in hydrogen, sulphur is lost and a mixture of silver and palladium subsulphide is formed.

R. Schneider obtained **palladic sulphide** or **palladium disulphide,** PdS_2, by melting together palladous sulphide with 12 times its weight of a mixture of equal parts of sulphur and sodium carbonate. Ammonium chloropalladate may be employed in place of palladous sulphide. The product is washed first with alcohol, and then with dil. hydrochloric acid, when the disulphide is left as a dark brown,

crystalline powder. H. G. Krall, and L. Wöhler and co-workers obtained the disulphide by the action of sulphur on palladium dichloride and sulphur at 450°. According to R. Schneider, the disulphide is stable in air; when heated in an inert gas like carbon dioxide, sulphur is sublimed, and palladous sulphide is produced, and later, the subsulphide. Nitric acid partially attacks the sulphur; and aqua regia dissolves it with the separation of sulphur. F. A. Bannister said that the stable existence of the disulphide is doubtful. L. Pauling and M. L. Huggins studied the sulphide space-lattice.

R. Schneider prepared **potassium sulphopalladate,** K_2PdS_3, by the decomposition of potassium thiopalladite in hydrogen. When the product is extracted with water, palladium is left behind, and the soln. contains the constituent elements in the proportions $K_2PdS_3.K_2S$. If palladous sulphide be heated with 12 times its weight of a mixture of equal parts of sodium carbonate and sulphur, and the cold mass extracted with water, **sodium sulphopalladate,** Na_2PdS_3, mixed with some sodium sulphate, passes into soln. Palladous dichlorodiammine may be used in place of palladous sulphide. If the sodium sulphopalladate be treated with silver nitrate, a brownish-black, crystalline powder of **silver sulphopalladate,** Ag_2PdS_3, is produced.

J. J. Berzelius[2] obtained **palladous sulphate,** $PdSO_4$, by boiling palladous nitrate with sulphuric acid. N. W. Fischer observed that palladium is not attacked by cold sulphuric acid, but the hot acid dissolves it with the evolution of sulphur dioxide and the formation of a yellowish-red soln. which, if saturated, deposits the normal sulphate as a red powder on cooling. A mixture of sulphuric and nitric acids was employed by R. J. Kane. N. W. Fischer dissolved hydrated palladous oxide in sulphuric acid. J. J. Berzelius observed that palladium dissolves in fused potassium hydrosulphate forming palladous sulphate. The salt can be dehydrated by heat without decomposition; at a red-heat it decomposes into sulphur trioxide and a subsulphate; and at a bright red-heat palladium is formed. The reddish-brown crystals deliquesce in moist air; and they are very soluble in water. R. J. Kane obtained a product $PdSO_4.7PdO.6H_2O$, by the hydrolysis of palladous sulphate in an excess of water. J. J. Berzelius reported a basic sulphate of palladium to be formed when palladous sulphide is roasted in air. W. Manchot and A. Waldmüller observed that palladous sulphate and dry nitric acid form **palladous dinitrosylsulphate,** $PdSO_4.2NO$. F. Müller and A. Reifkohl studied the solubility of palladous sulphate in N-Na_2SO_4.

H. Müller prepared **palladous sulphatodiammine,** $[Pd(NH_3)_2SO_4]$, by treating the corresponding dihydroxydiammine with sulphuric acid, or by the action of silver sulphate on the dichlorodiammine. The orange-yellow octahedra are soluble in cold water, and precipitated from the aq. soln. by hydrochloric acid. The salt is stable up to 150°. R. J. Kane obtained **palladous tetramminosulphate,** $[Pd(NH_3)_4SO_4].H_2O$, by the action of hot sulphuric acid on the corresponding hydroxide, or by treating the sulphatodiammine with a large excess of ammonia. It is also formed when a soln. of palladous sulphate is treated with ammonia. The colourless crystals are soluble in water, insoluble in alcohol, and readily dehydrated by heat. Hydrochloric acid precipitates the dichlorodiammine from the aq. soln. K. A. Jensen prepared **palladous thiocarbazidosulphate,** $[Pd(thio)_2]SO_4$.

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§ 13. Palladium Carbonates, Nitrates, and Phosphates

The simple **palladium carbonate** has not been prepared, but H. Müller [1] obtained **palladous carbonatodiammine,** $[Pd(NH_3)_2CO_3]$, by the action of carbon dioxide on a soln. of the hydroxide; by the action of silver carbonate on a soln. of the chloride; and by the action of barium carbonate on a soln. of the sulphate. The filtrate furnishes golden-yellow octahedra which are readily soluble in water. The aq. soln. has an alkaline reaction, and it gives precipitates with salts of barium, calcium, copper, and silver. H. Müller prepared **palladous tetramminocarbonate,** $[Pd(NH_3)_4]CO_3$, by saturating a soln. of the corresponding hydroxide with carbon dioxide; by the action of silver carbonate on the chloride; by the action of barium carbonate on the corresponding sulphate; and by heating to 40° to 50°, a soln. of the corresponding cyanate. The colourless, prismatic crystals are soluble in water, and at 100° form a yellow salt. The aq. soln. is alkaline and gives precipitates with salts of barium, calcium, copper, and silver.

W. H. Wollaston [2] observed that palladium dissolves more slowly in nitric acid than in nitric acid containing some nitrous acid. N. W. Fischer, and R. J. Kane obtained **palladous nitrate,** $Pd(NO_3)_2$, by dissolving palladium in nitric acid of sp. gr. 1·35 to 1·40, evaporating the soln. to a syrupy consistency, and cooling. The salt crystallizes in brownish-yellow, rhombic prisms; they are very deliquescent, and cannot be perfectly dried. The salt is very soluble in water, yielding a soln. which is readily hydrolyzed to form a brown basic nitrate. J. J. Berzelius observed that when the salt is heated, it furnishes successively a basic nitrate, palladous oxide, and finally the metal. A. Mailfert observed that ozone converts the nitrate into peroxide. W. Manchot and A. Waldmüller found that palladous nitrate takes up nitric oxide additively, and this is immediately oxidized by the nitrate radicle so that palladous nitrite is formed. G. Scagliarini and G. B. Berti-Ceroni found that when the soln. is heated with a conc. soln. of ammonium or potassium persulphate, a palladic hydroxide is formed. A. Ditte observed coloured precipitates with stannous salts.

H. Müller could not isolate **palladous dinitratodiammine,** $[Pd(NH_3)_2(NO_3)_2]$, but he obtained a yellow soln. by the action of silver nitrate on a soln. of the corresponding chloride. When the soln. is evaporated, it furnishes a brown solid which detonates violently when heated. The solid ammine is not obtained by treating palladous nitrate with ammonia. A. Gutbier and C. Fellner prepared **palladous dinitratobispyridine,** $[Pdpy_2(NO_3)_2]$, in golden-yellow crystals; and **palladous dinitratobispicoline,** $[Pd(C_5H_4(CH_3)N)_2(NO_3)_2]$, in golden-yellow crystals.

J. J. Berzelius, H. D. K. Drew and co-workers, and N. W. Fischer obtained **palladous tetramminonitrate,** $[Pd(NH_3)_4](NO_3)_2$, by adding to a soln. of palladous nitrate aq. ammonia until the precipitate which first forms has all dissolved, and then evaporating the soln. for crystallization. The product is mixed with some ammonium nitrate in quantity proportional to the acidity of the original soln. of nitrate. The ammonium nitrate is easily removed by virtue of its deliquescence, and easy solubility in water. The salt was also prepared by R. J. Kane. The transparent, colourless, four-sided prisms and plates, melt when heated, and then detonate slightly with a flash. The salt is decomposed by hydrochloric acid

with the slow separation of the corresponding chloride ; it is easily soluble in water ; it forms a yellow soln. with nitric acid ; a colourless soln. with ammonia : and it is insoluble in alcohol.

No **palladium phosphate** has been prepared.

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CHAPTER LXXII

OSMIUM

§ 1. The Occurrence of Osmium

THE history of osmium has been indicated in connection with the platinum metals. Osmium occurs in nature associated with the platinum metals. Thus, F. Wöhler [1] reported 3 per cent. of osmium in laurite from Borneo; L. F. Svanberg reported 0·19 to 0·97 per cent.—of osmium not as osmiridium—in platinum ores from Choco, Equatorial Colombia; H. St. C. Deville and H. Debray, 0·05 to 1·25 per cent.; T. Thomson, 24·1 per cent. in ore from Brazil; F. Weil, 0·81 per cent. in platinum from California; and S. Kern found up to 0·60 in ore from Russia. I. Koifman found 0·79 to 20·13 per cent. of osmium present as osmiridium in native platinum from various mines in the Urals. Here, the osmium is also present in association with iridium as the mineral **osmiridium.** Thus, J. J. Berzelius reported 1·40 to 2·30 per cent. of osmiridium in some Russian platinum ores; H. St. C. Deville and H. Debray, 0·50 to 2·35 per cent.; G. Osann, 0·11 to 1·80 per cent. L. Duparc and M. N. Tikonowitch, and N. Wissotsky found 0·71 to 3·97 per cent. in ores from Tagil; 0·61 to 5·85 per cent. in ores from the water-shed of the river Iss-Swetli-Bor, and Weressowy-Ouwal; 0·79 to 20·21 per cent. in ores from Kamenouchky, Koswinsky, Kanjakowsky, Omountnaïa, and Daneskin-Kamen; 0·18 to 3·10 per cent. in ore from Goussewi-Kamen, Kiedrowka, Barantcha, and Solwa; and 0·28 to 1·89 per cent. in ore from Goussewka, Schoumika, and Obleiskaya-Kamenka. L. F. Svanberg reported 1·56 to 1·91 per cent. of osmiridium in Colombian ores, and H. St. C. Deville and H. Debray, 0·95 to 7·90 per cent. in ores from the same locality; M. Böcking, 3·80 per cent. in ore from Borneo, and S. Bleekrode, 0·34 per cent.; H. St. C. Deville and H. Debray, 1·10 to 7·55 per cent. in ores from California; F. Weil, 27·65 per cent.; A. Kromayer, 22·55 per cent.; S. Kern, 0·11 to 2·80 per cent.; and C. Claus, 22·55 per cent.; H. St. C. Deville and H. Debray reported 37·30 per cent., and W. J. Martin, 24 to 94 per cent. in ores from Oregon, 2·85 per cent. in an ore from Spain, and 25·0 to 26·0 per cent. in ores from Australia; J. C. H. Mingaye, 9·30 per cent. in ore from New South Wales; and H. S. Elford, and P. O. Lennon, in Tasmanian ores. G. C. Hofmann observed 3·77 to 14·62 per cent. in ores from British Columbia, Canada. The occurrence of osmium was discussed by V. M. Goldschmidt and C. Peters, R. A. Cooper, and J. R. Thurlow; and the structure, by O. E. Zvjagintseff and co-workers.

Osmiridium thus occurs in Choco, Colombia; Urals, Russia; the auriferous drifts, New South Wales, Australia; auriferous beach sands of North California, U.S.A.; in the gold washings of some rivers in British Columbia, Canada; in the dunites and norites of South Africa; etc.—*vide* platinum. The composition of the osmiridiums is discussed in connection with the occurrence of platinum—*vide infra.* The varieties with under about 60 per cent. of iridium have been called **syserskite** or osmiridium in contrast with **iridiosmium,** or **nevyanskite** for varieties with over about 60 per cent. of iridium. The line of demarcation is ill-defined. F. Wöhler also reported the presence of about 3·03 per cent. of osmium in *laurite.* R. Hermann, J. J. Berzelius, and G. A. Kenngott described a black magnetic substance in some gold mines of the Urals; it was called *irite,* and was shown by C. Claus to be an iridiosmium associated with chromite and iron oxides.

O. E. Zvjagintseff isolated **aurosmirid,** a solid soln. of gold, osmium, and ruthenium in iridium in the residue remaining after dissolving platinum in aqua regia. It has a cubic space-lattice.

The general occurrence of osmium has been discussed in connection with the platinum metals. F. W. Clarke and H. Washington's [2] estimate of the proportion in the igneous rocks of the earth's crust is of the order $n \times 10^{-10}$ per cent.; and I. and W. Noddack gave $6{\cdot}0 \times 10^{-12}$ for the earth's crust; $8{\cdot}8 \times 10^{-6}$ for meteoric iron; $1{\cdot}0 \times 10^{-5}$ for troilite; and for the atomic distribution, oxygen unity, $1{\cdot}4 \times 10^{-6}$, and later they gave $3{\cdot}2 \times 10^{-8}$ for the earth's crust, and $3{\cdot}9 \times 10^{-6}$ for meteorites. The subject was discussed by P. Niggli, P. Vinassa, and F. Bernauer. M. N. Saha, and H. A. Rowland classed osmium amongst the elements whose spectral lines are of doubtful occurrence in the solar spectrum; and, according to H. von Klüber, the presence of the spectral lines of osmium in the spectra of the fixed stars is doubtful.

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§ 2. The Extraction and Preparation of Osmium

The opening up of platinum ores with aqua regia is discussed in connection with platinum. Osmium can be relatively easily isolated and obtained in a high degree of purity owing to the formation of a volatile osmium tetroxide, or in soln., osmic acid. The distillation of the tetroxide from a soln. strongly acidified with nitric acid, is a simple and direct way of separating osmium from the other platinum metals, and in the absence of halogen acids, from all other metals. In the methods described by J. J. Berzelius,[1] L. N. Vauquelin, and W. H. Wollaston for opening up the platinum metals with hot aqua regia, in a retort, the osmium collects in the distillate as osmic acid; and, according to A. Laugier, the osmium can be recovered by nearly neutralizing the acid liquor with milk of lime, and distilling to dryness.

The distillate containing the osmic acid is mixed with a moderate excess of hydrochloric acid and decomposed by zinc, the black flakes of osmium are collected, washed with water acidulated with sulphuric acid, then with water, and dried at a gentle heat. If too much hydrochloric acid is used, a purple liquid is formed, and if too little, some osmic acid will escape reduction. J. J. Berzelius suggested that some osmic acid escapes with the hydrogen gas.

The grains of osmiridium resist the attack of aqua regia, and the grains are so hard that pulverization is difficult. H. St. C. Deville and H. Debray recommended heating the osmiridium with 8 to 10 times its weight of zinc, and subsequently removing the zinc by hydrochloric acid or by heat. W. H. Wollaston heated the mineral with a mixture of potassium hydroxide and nitrate. E. Frémy, C. Claus, O. W. Gibbs, and A. Guyard heated the osmiridium with 3 times its weight of potassium nitrate—and observed that a little osmium is lost by volatilization. Fusion processes with alkali and potassium nitrate were also used by A. Gutbier and K. Trenker, F. Krauss and H. Kükenthal, and A. Joly and H. Debray; alkali hydroxide and permanganate, by O. Ruff and F. Vidic; alkali and potassium chlorate, by J. Fritzsche and H. Struve, C. Claus, and V. Antony and A. Lucchesi; and sodium dioxide, by J. L. Howe, E. Leidié and L. Quennessen, and E. Wichers and co-workers—*vide* ruthenium. J. Persoz heated to redness 1 part of osmiridium with 2 parts of dry sodium carbonate, and 3 parts of sulphur, and the method was examined by R. A. Cooper, F. Döbereiner, L. R. von Fellenberg, C. Claus, and O. W. Gibbs. F. Wöhler, J. R. Joss, J. J. Berzelius, C. Claus, and W. von Schneider heated to redness a mixture of the ore with sodium chloride in a current of chlorine; and F. Wöhler made osmiridium the anode in a soln. of sodium hydroxide and observed that sodium osmate and ruthenate are formed.

H. St. C. Deville and H. Debray found that the mineral is attacked when it is heated with barium dioxide. E. Leidié and L. Quennessen recommended heating the mineral with sodium dioxide as indicated in connection with other platinum metals. E. Wichers and co-workers said:

The best method of attack for crude iridium, or its native alloys with osmium, is to fuse with an alkaline oxidizing mixture such as potassium hydroxide and nitrate, sodium hydroxide and dioxide, or barium dioxide with or without barium nitrate. Treatment with the last-named reagents is not strictly a fusion, as the mass sinters rather than melts, thus permitting greater latitude in the choice of crucibles. Metal crucibles are but slightly attacked and the heating may be done in clay crucibles. If desired, the barium salts can easily be separated from the resulting iridium soln. by precipitation as barium sulphate. Potassium salts usually are to be avoided because of the precipitation of potassium chloroiridate when the iridium is finally converted to chloride. Fusion with 3 parts by weight of sodium hydroxide and 1 part of sodium dioxide, preferably in a silver dish, otherwise in nickel or a thick-walled iron vessel, is probably as convenient and satisfactory a method as any. In the fusion of crude osmium or osmiridium with sodium hydroxide and sodium dioxide, as described in the section on iridium, the soln. obtained by leaching the melt with water contains osmium as sodium osmate, Na_2OsO_4, and also contains ruthenium and small amounts of the other platinum metals. Certain base metals, such as tin, lead, and zinc, may also be present.

The receiver for the osmic acid usually contains some alkaline liquid. R. Gilchrist observed that if the soln. contains 40 per cent. of nitric acid by volume, no ruthenium is volatilized. According to E. Wichers and co-workers, the aq. extract from the fusion with sodium hydroxide and dioxide contains practically all the osmium, a large proportion of the ruthenium, and some iridium. The alkaline soln. of osmium and ruthenium is transferred to a suitable distilling flask, strongly acidified with nitric acid, and gradually heated to the b.p. whilst a current of air is passed through the liquid, as recommended by M. C. Lea, so as to carry the vapours of osmium tetroxide into a chain of recurring flasks. These flasks contain a 10 to 12 per cent. of sodium hydroxide. A little alcohol is added to all but the first one. When no more osmium tetroxide distils, as may be observed by putting a fresh soln. in the first receiving flask, the contents of the several flasks are combined and digested to insure the reduction of all osmium tetroxide to sodium

osmate. More alcohol is added if needed. Practically all of the osmium may be separated from the ruthenium in this distillation. It has been observed, however, that it is not possible in this way to effect a complete separation of osmium from soln. to which alcohol has been added.

To separate the osmium from the alkali osmate soln., L. N. Vauquelin reduced the soln. of the tetroxide by hydrochloric acid and zinc as just indicated ; J. J. Berzelius used mercury, and distilled mercury from the resulting amalgam ; and F. Döbereiner used an alkali formate as reducing agent. J. J. Berzelius reduced the tetroxide in a current of hydrogen ; H. St. C. Deville and H. Debray used a mixture of carbon monoxide and dioxide, or simply carbon, when the metal is obtained in a crystalline state. J. J. Berzelius, E. Frémy, and R. Schneider obtained the metal by decomposing the ammines by heat. H. St. C. Deville and H. Debray, and E. C. Fritzmann recommended precipitating the osmium from the alkaline liquid by sodium sulphide. S. Tennant saturated the soln. with hydrogen sulphide, and heated the sulphide to a high temp. in a closed carbon crucible. The osmium collected as metal in the upper part of the crucible.

H. Moraht and C. Wischen recovered the osmium by electrolyzing the alkali osmate soln. when osmium dioxide collects on the cathode. O. Ruff and F. Bornemann recommended exactly neutralizing the soln. with sulphuric acid which produces a precipitate of hydrated osmium dioxide. The soln. is digested for some hours on a steam-bath to coagulate the precipitate and hinder its tendency to deflagrate when afterwards ignited. The dried precipitate is reduced in hydrogen. The product is almost free from platinum, but traces may be present owing to a mechanical transport from the distilling flask. Traces of alkali, iron, and silica, derived from the sodium hydroxide soln., may also be present.

R. Gilchrist and co-workers further purified the osmium by burning it to sodium tetroxide in a current of oxygen. E. Wichers and co-workers thus described the operation :

The metal was heated in boats in a hard glass tube in an electric furnace. Half of the combustion tube was bent downward at an angle of 45° and the end of the tube held in an open flask containing enough hydrochloric acid of sp. gr. 1·12 to seal the opening of the tube. The receiving flask was cooled with ice. When the temp. of the furnace reached 220° to 230°, a vigorous reaction occurred, accompanied by a rapid absorption of oxygen and a progressive glowing of the metal. The product was a black powder of greater bulk than the metal, and was presumably the dioxide. At this stage it was necessary to supply oxygen rapidly to avoid a diminished press. in the tube. After this reaction had subsided, the temp. was raised gradually, whereupon the material in the boats oxidized quietly to the tetroxide. The latter condensed to a solid in the cool portion of the tube. When all of the metal was converted to the tetroxide the solid cake was transferred to the receiving flask by gently warming the tube until the mass loosened and dropped into the flask. A modification of this method, in which the hydrochloric acid is omitted and the receiving flask is cooled in a freezing mixture, may be used if osmium tetroxide is the desired product. The contents of the receiving flask were quickly transferred to a flask fitted with a reflux condenser, only ground-glass joints being used. To this flask hydrochloric acid of sp. gr. 1·12 and a little alcohol were added. The flask was warmed gently, and the temp. raised gradually to incipient boiling in about 3 hrs. The osmium tetroxide was gradually reduced to quadrivalent osmium chloride, the completion of the reaction being shown by the absence of droplets of osmium tetroxide condensing on the walls of the flask, by the change in colour of the soln. to a clear, transparent red, and by the absence of the characteristic odour of osmium tetroxide. The end of the reflux condenser was fitted with a trap containing a soln. of sodium hydroxide and alcohol to catch the small amount of osmium tetroxide which passed the condenser. Twice the theoretical amount of hydrochloric acid required to form H_2OsCl_6 was used. A similar reaction was used for the preparation of bromoösmic acid, H_2OsBr_6. When hydrobromic acid is used, alcohol is not needed, but may be used to hasten the reduction of the tetroxide. The soln. containing chloroösmic acid was evaporated on the steam-bath without loss of osmium. It was necessary to keep the soln. distinctly acidic to prevent the precipitation of a basic compound, presumably the hydrated dioxide. Ammonium chloroösmate was precipitated from this soln. by the addition of ammonium chloride. The salt is brick-red in colour and is relatively insoluble. The salt was ignited to metal in a current of hydrogen, a temp. of 600° to 700° being finally attained. The hot sponge was cooled in oxygen-free nitrogen. This metal, preserved in a stoppered bottle, did not for some days begin to emit the odour of osmium tetroxide,

Finely-divided osmium unites with oxygen to form the tetroxide even at ordinary temp. Osmium allowed to cool in hydrogen glows when brought into contact with air, thereby causing some loss of osmium as the tetroxide. A further purification, if thought necessary, can be accomplished by repeating the cycle of operations just described, beginning with the sponge obtained by the ignition of the ammonium chloroösmate. Osmium remaining in the filtrates from the precipitation by ammonium chloride can be recovered by evaporating the soln. to dryness and igniting the entire residue under hydrogen.

A. Gutbier found that in working up osmium residues containing organic substances, the metal is not converted into the chloride when treated with chlorine, and in consequence the purification of the metal could not be effected in the usual way by means of the insoluble ammonium chloro-osmate. The following method has been evolved for the recovery of the metal from such residues. The dried residues are placed in porcelain boats in a hard glass tube, heated, and a current of oxygen is passed over; this burns away all carbonaceous matter, and the osmium is converted into the tetroxide, which distils over into a series of U-tubes containing various reducing agents. As reducing agents, the author employs alcohol in slightly alkaline soln., ammoniacal alcohol containing ammonium chloride and an alcoholic soln. of hydrazine hydrate. The reduced soln. is evaporated to dryness on the water-bath, and then converted into the metal by heating in hydrogen and allowing to cool in carbon dioxide. By this process, it is possible to recover 2·83 grms. of osmium from an artificially-prepared mixture containing 3·0 grms. of osmium.

H. St. C. Deville and H. Debray reported **crystalline osmium** to be formed by heating to redness osmium mixed with 7 to 8 times its weight of tin (or zinc), in a carbon crucible, and allowing the mass to cool slowly. This product is then treated with hydrochloric acid when pseudomorphs after the crystalline stannide remain. H. Debray obtained octahedral crystals by melting osmium with pyrite, and borax and extracting the product with dil. hydrochloric acid. It is assumed that osmium sulphide is formed and decomposed in the operation. F. Döbereiner obtained **osmium black,** or rather a bluish-black, powder of finely-divided osmium, by reducing aq. soln. of osmium salts, or of osmium tetroxide by an alkali formate. A. A. Pollitt discussed osmium as a catalytic agent. G. R. Levi and R. Haardt discussed the structure of the powder. S. G. S. Dicker prepared **osmium films** by the thermal decomposition of a carbonyl. E. Cohen and T. Strengers did not obtain **explosive osmium** by the action of acid on the zinc-osmium alloy.

A. Gutbier and G. Hofmeier [2] prepared **colloidal osmium,** or **osmium hydrosol,** by reducing a soln. of potassium osmate with hydrazine in the presence of gum arabic as protective colloid. N. Castoro used acrolein as reducing agent; O. Makowka, a soln. of acetylene in acetone; and C. Paal and C. Amberger used sodium lysalbate and protalbate as protective colloids. C. Amberger reduced potassium osmate with hydrazine hydrate suspended in lanolin as protective colloid; and then dissolved the resulting osmium dioxide hydrosol in petroleum, precipitated it with alcohol, and reduced it in hydrogen at 50° to 60°. A hydrosol with 21 per cent. osmium was obtained in this manner. J. Donau found that a borax bead is coloured reddish-brown by osmium.

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§ 3. The Physical Properties of Osmium

The **colour** of osmium in a compact state is bluish-grey; and when precipitated in a fine state of subdivision, it is bluish-black. H. St. C. Deville and H. Debray[1] obtained the **crystals** in a microscopic cube, *en trémies*. The hexagonal form of osmiridium or iridosmium was taken by G. Rose, and A. Lévy to represent a dimorphic form, but W. Prinze showed that the so-called hexagonal forms of all the varieties he examined are distorted octahedra belonging to the cubic system. A. W. Hull found that the **X-radiograms** correspond with a closely packed hexagonal lattice with the side of unit triangle, a=2·714 A., the height of unit triangle, c=4·32 A., and the axial ratio, $a:c$=1 : 1·59; G. Aminoff and G. Phragmen gave a=2·90 A., c=4·60 A., and $a:c$=1 :·1·590; T. Barth and G. Lunde, a=2·714 A., c=4·314 A., and $a:c$=1:1·584; O. E. Swjaginzeff and B. K. Brunowsky, a=2·716 A., and c=4·331 A.; G. R. Levi and R. Haardt, a=2·714 A., c=4·316 A.; and E. A. Owen and co-workers, a=2·7304 A., and c=1·5785 A.; and $a:c$=1 : 1·590. The subject was discussed by R. W. G. Wyckoff.

H. St. C. Deville and H. Debray gave 21·40 and 22·477 for the **specific gravity** of osmium; A. Joly and M. Vezes gave 22·48 for the fused metal. J. J. Berzelius observed 7 to 10 for the sp. gr. of the pulverulent metal; and R. Gilchrist gave 19·13 for osmium sponge. G. R. Levi and R. Haardt calculated from the X-radiogram data that the sp. gr. of osmium is 22·98 when the best representative value from the observed data is 22·48; E. A. Owen and co-workers calculated 22·61 at 18°, when 22·41 was the observed value. V. M. Goldschmidt calculated 1·336 A. for the **atomic radius.** E. H. Westling, J. C. Slater, G. Hägg, and W. Biltz and K. Meisel studied the packing density; and W. Hulme-Rothery, J. A. M. van Liempt, and L. Pauling, the atomic constants. The metal is very hard; I. R. Rydberg gave 7·0 for the **hardness** on Mohs' scale. E. Widder gave for the **elastic modulus,** $E=E_{20}\{1-0·0004032(\theta-20)\}$.

H. Fizeau [2] found the coeff. of **thermal expansion** of osmium to be $\alpha=0{\cdot}0_5657$ at 40°, and $0{\cdot}0_5679$ at 50°. E. A. Owen and co-workers gave $6{\cdot}1\times10^{-6}$ for the mean coefficient of expansion. H. V. Regnault observed the **specific heat** of osmium to be from 0·03063 to 0·03113 between 18° and 98°; J. Dewar found 0·0078 between −253° and −196°; and F. M. Jäger and E. Rosenbohm gave for the sp. ht. and the at. ht.:

	0°	100°	200°	400°	600°
c_p . . .	0·3099	0·03146	0·03193	0·03287	0·03382
C_p . . .	5 915	6·006	6·096	6·276	6·455
	800°	1000°	1200°	1400°	1600°
c_p . . .	0·03476	0·03571	0·03665	0·03759	0·03854
C_p . . .	6·636	6·817	6·996	7·176	7·358

The relation between sp. ht. and temp. is linear $c_p=0{\cdot}030986+0{\cdot}0_54721\theta$; and for the at. ht., $C_p=5{\cdot}9152+0{\cdot}0009019$. The at. ht. exceeds the theoretical $3R$, at 100°, and at 1600°, it is 7·358. F. M. Jäger observed no sign of any allotropic change. A. H. Stuart discussed the relation between the elastic constants and the sp. ht.

J. L. Byers studied the behaviour of the metal on cupellation. S. Tennant said that osmium does not fuse or volatilize when heated to whiteness in a hollow in a piece of charcoal. Osmium was for a long time considered to be infusible. H. St. C. Deville and H. Debray believed that they fused and volatilized some in the oxyhydrogen flame; A. Joly and M. Vezes melted the metal in the electric arc furnace; and H. Moissan melted and distilled the metal in the electric arc furnace. The metal oxidizes, forming a volatile oxide when heated in air, and H. St. C. Deville and H. Debray said that the compact metal can be heated to 419° without volatilization. R. Pictet estimated the **melting point** to be 2500°; W. Guertler and M. Pirani, F. E. Carter, and W. R. Mott, 2700°; and H. Moissan, and A. Joly and M. Vezes, 2200° to 2600°. W. R. Mott estimated the **boiling point** to be 5100°. According to W. Crookes, if the rate of volatilization of platinum in air at 1300° is 2, that of osmium is 100. J. W. Richards estimated the **heat of fusion** to be 35 Cals. A. D. van Riemsdijk observed no flashing in cupellation. G. N. Lewis and co-workers gave 7·8 to 8·4 Cals. for the **entropy** of osmium at 25°; and E. D. Eastman gave 7·8 to 9·0 Cals. The internal energy and entropy were studied by R. D. Kleeman, and K. K. Kelley. J. J. van Laar discussed the **equation of state.**

A. L. Hilgott,[3] and F. Leder studied the radiation from osmium at different temp.

According to W. Frazer,[4] the **flame spectrum** of osmium has three strong lines, and one feeble line in the blue-violet, and A. Gouy studied the spectra of flames charged with powdered salts of osmium. The spark spectrum of osmium has some feeble lines, with the 4420·6 line in the indigo-blue the most prominent. The more important lines in the spark spectrum are 2909·19, 3772·71, 4135·95, 4261·01, and 4420·62. The **spark spectrum** was studied by W. Huggins, R. Thalén, F. McClean, E. Demarçay, F. Exner and E. Haschek, W. E. Adeney, A. Hagenbach and H. Konen, and J. M. Eder and E. Valenta. L. H. G. Clark and E. Cohen, and W. F. Meggers and O. Laporte studied the under-water spark spectrum. The more important lines in the **arc spectrum** are 3752·69, 3782·34, 3794·08, 3963·80, 3977·39, 4112·19, 4135·96, 4173·40, 4212·06, 4261·01, and 4420·64. The arc spectrum was studied by J. N. Lockyer, H. A. Rowland and R. R. Tatnall, W. F. Meggers, W. Albertson, H. Kayser, F. Exner and E. Haschek, A. Hagenbach and H. Konen, and J. M. Eder and E. Valenta. The effect of *pressure* on the spectral lines was studied by W. J. Humphreys; and the effect of a *magnetic field*—the Zeeman effect—by B. E. Moore; and the *structure* of the spectral lines, by P. G. Nutting, E. Paulson, and A. Dauvillier. W. Gerlach and K. Ruthardt discussed the most sensitive lines for the recognition of osmium. J. Formanek examined the **absorption spectra** of aq. soln. of the salts. The brownish-yellow, conc. soln. of osmium chloride has bands in the green, blue, and violet; there are

no bands with dil. soln.; and soln. of osmium chloride give no characteristic reaction with tincture of alkanna. R. Samuel and A. R. R. Despande studied the absorption spectra of soln. of the salts, and A. Langseth and B. Qviller, the *ultra-violet absorption spectrum.*

The **X-ray spectrum** was examined by F. K. Richtmyer and S. Kaufman,[5] H. G. J. Moseley, K. Lang, J. E. Mack and J. M. Cork, B. Polland, and M. Siegbahn; and A. Sommerfeld gave for the K-series lines corresponding with $\alpha_1\alpha=0{\cdot}19645$; $\alpha_2\alpha'=0{\cdot}20131$; $\beta_1\beta=0{\cdot}17361$; and $\beta_2\gamma=0{\cdot}16875$. M. Siegbahn, A. Sommerfeld, H. Hirata, and B. R. Stephenson and J. M. Cork, gave for the L-series, $\alpha_1\alpha=1{\cdot}38816$; $\alpha_2\alpha'=1{\cdot}3982$; $L_{I}=0{\cdot}9516$; $L_{II}=0{\cdot}9985$; $L_{III}=1{\cdot}138$; $\beta_1\beta=1{\cdot}19459$; $\beta_2\gamma=1{\cdot}16838$; $\beta_3\phi=1{\cdot}772$; $\beta_4\phi=1{\cdot}2150$; $\beta_5\xi=1{\cdot}140$; $\beta_6\iota=1{\cdot}2048$; $\beta_9=1{\cdot}1238$; $\gamma_1\delta=1{\cdot}02247$; $\gamma_5K=1{\cdot}0541$; and $\gamma_6\theta=1{\cdot}0053$. The structure was studied by D. Coster, J. C. Bryce, E. Hjalmar, A. Sandström, F. K. Richtmyer and S. Kaufman, J. Zahradnicek, A. Dauvillier, G. Réchou, K. Lang, and P. Auger and A. Dauvillier. M. Siegbahn, and A. Sommerfeld gave for the M-series, $M_{I}=4{\cdot}137$; $M_{II}=4{\cdot}412$; $M_{III}=5{\cdot}027$; $M_{IV}=5{\cdot}975$; $M_{V}=6{\cdot}194$; $\gamma=4{\cdot}7799$; $\eta=5{\cdot}802$; $\delta=4{\cdot}949$; $\epsilon=6{\cdot}882$; $\gamma'=5{\cdot}717$; $\gamma\gamma=5{\cdot}669$; $N_{II}-M_{IV}=8{\cdot}342$; $\beta\beta=6{\cdot}253$; $N_{III}-M_{V}=8{\cdot}291$; $\alpha_1\alpha=6{\cdot}476$; $\alpha'=6{\cdot}438$; $\alpha''=6{\cdot}457$; $\beta'=6{\cdot}232$; $\beta''=6{\cdot}233$; and $\gamma'=5{\cdot}652$. The M-series was also studied by R. A. Rogers, E. G. Purdom and J. M. Cork, and E. Lindberg, and the N-series by E. Lindberg, and T. Magnusson. S. K. Allison studied the electron levels of the X-ray spectra; and E. Fermi and co-workers, the artificial radioactivity.

T. Pavolini[6] studied the photosensitivity; E. Amaldi and co-workers, and F. W. Newman and H. J. Walke, the induced radioactivity; and N. Piltschikoff, the Moser rays.

F. Blau[7] found the sp. **electrical conductivity** of osmium to be $10{\cdot}5\times10^4$ mhos per cm. cube at 20°; and L. Lombardi found the temp. coeff. of the resistance to be $a=0{\cdot}00420$. A. Schulze studied the subject; and F. Simon, the theory of conductivity.

E. G. Weischede[8] found that in a soln. of potassium chloro-osmate acidified with sulphuric acid containing 16 mgrms. of osmium, per 100 c.c. at 20°, the **electrode potential** was 0·439 volt; and in the electrolysis of the soln., he observed that the **deposition potential** of osmium was 0·023 to $-0{\cdot}11$ volt, the current density 10^{-5} per sq. cm. J. A. V. Butler and co-workers studied the oxidation potential; and A. Thiel and W. Hammerschmidt, the hydrogen over-voltage. W. R. Crowell and co-workers determined quadrivalent osmium by electrometric titration.

M. Faraday[9] made some observations on the magnetic properties of osmium. K. Honda gave for the **magnetic susceptibility** $0{\cdot}04\times10^{-6}$ between 18° and 1100°; M. Owen gave $0{\cdot}048\times10^{-6}$ mass unit; and K. Honda and T. Sone, $0{\cdot}074\times10^{-6}$ mass unit. B. Cabrera and A. Dupérier gave $Os^{\cdot\cdot}=82{\cdot}75\times10^{-6}$ c.g.s. unit. A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility increases with temp. up to 427°. P. Weiss studied the magnetic moment. F. H. Loring studied the subject.

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§ 4. The Chemical Properties of Osmium

P. M. Niccolini [1] discussed the odour of the element. E. Müller and K. Schwabe [2] observed that the **hydrogen** taken up by osmium is all irreversibly absorbed indicating chemical combination. A. Gutbier and W. Schieferdecker found that the absorption power of osmium for hydrogen, Fig. 1, closely resembles that of iridium. V. S. Sadikoff and A. K. Michailoff studied osmium as a catalyst in hydrogenation reactions. J. J. Berzelius observed that osmium does not oxidize in the cold or at 100° in **air,** or in **oxygen,** but at a higher temp. oxidation occurs; but, according to H. Rose, and H. St. C. Deville and H. Debray, finely-divided osmium has a perceptible smell at ordinary temp. presumably owing to the formation of a volatile oxide; and when exposed to air, it darkens the walls of the vessel in which it is confined. F. E. Carter said that finely-divided osmium begins to oxidize in air at 100°, forming the tetroxide; but massive osmium does not oxidize appreciably below redness. H. von Wartenberg said that the limiting quantity which can be detected by the sense of smell is 2×10^{-5} mgrm. per c.c. R. Willstätter and E. Sonnerfeld observed that colloidal osmium readily oxidizes at ordinary temp. R. Gilchrist observed that metallic osmium which has been ignited and cooled in hydrogen is readily attacked by air to form osmium tetroxide; in some cases the spongy osmium glows. This can be prevented by displacing the hydrogen with nitrogen. Crystalline or fused osmium is stable at ordinary temp. and, according to H. St. C. Deville and H. Debray, it commences to oxidize at 400°; and, according to O. Sulc, oxidation begins at 200° in air, and at 160° in oxygen. M. Vèzes added that temp. of oxidation depends on the state of subdivision of the metal. F. Wöhler observed that when osmium is employed as anode in the electrolysis of an acidic or alkaline soln. it is converted into a peroxide. P. L. Dulong and J. L. Thénard observed that finely-divided osmium causes a mixture of oxygen and hydrogen to unite explosively at 40° to 50°; F. C. Phillips found that the platinum metals have catalytic activities in the decreasing order Os, Pd, Pt, Ru, Ir, Rh, and Au in oxidizing hydrogen; and H. Remy and B. Schäfer found osmium to be inactive. H. Remy and H. Gonnington studied the subject. K. A. Hofmann and O. Schneider found that the activity of the platinum metals in oxidizing hydrogen in the presence of chlorate soln. decreased in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag. C. Paal and C. Amberger placed the colloidal metals in the decreasing order of activity in decomposing **hydrogen dioxide:** Os, Pd, Pt, and Ir. G. R. Levi studied the subject. According to H. V. Regnault, and C. Claus, osmium is oxidized by the vapour of **water.**

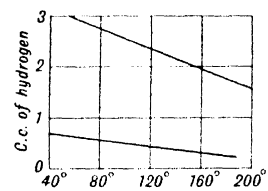

FIG. 1.—Isobars of the System: $Os-H_2$.

According to H. Moissan, **fluorine** does not attack pulverulent osmium in the cold, but union commences near 100°, and the heat of the reaction makes the metal incandescent. O. Ruff and F. Eisner observed that various fluorides are formed. O. Ruff and F. W. Tschirch observed that combination occurs at about 250°, and osmium tetra-, hexa-, and octo-fluorides are formed. According to

J. J. Berzelius, **chlorine** does not act on osmium in the cold, but when the dry gas is passed over the metal heated in a long tube a dark green sublimate is formed of the dichloride, and further on, a red sublimate of the tetrachloride. C. Claus, O. Ruff and K. Bornemann, and H. Moraht and C. Wischin observed that the tetrachloride is formed at 650° to 700°. The attack is completed, said J. J. Berzelius, only when the metal is mixed with an alkali chloride, and a chloro-osmate is formed. A. Joly noted that a mixture of carbon monoxide and chlorine gives no better results than does chlorine alone. O. Ruff and H. Krug observed that **chlorine trifluoride** attacks the metal with incandescence. H. Moraht and C. Wischin observed that **bromine** vapour is without action on the metal alone or admixed with a bromide; and L. N. Vauquelin, and H. Moraht and C. Wischin, that **iodine** vapour is without action on the metal alone or mixed with an iodide. W. A. Dudley, A. M. Vasileff, and C. Matignon observed that **hydrochloric acid** does not attack osmium, but in the presence of oxygen the metal is dissolved by this acid. A soln. of **potassium hypochlorite** readily attacks the finely-divided metal.

J. J. Berzelius, and H. St. C. Deville and H. Debray observed that osmium burns brightly in the vapour of **sulphur**, with the evolution of heat and light, to form a sulphide. G. R. Levi and M. Faldini observed that the presence of osmium decreased the activity of platinum as a catalyst in the oxidation of **sulphur dioxide.** Osmium is attacked by hot, conc. **sulphuric acid.** K. Hradecky found that cold **selenic acid** has no action on osmium, but at 150°, the metal dissolves; the colourless soln. contains selenious acid and osmium tetroxide. E. A. Arnold and R. E. Burk studied the catalytic effect of osmium on the thermal decomposition of **ammonia.** F. Haber and co-workers found osmium to be a very effective catalyst in the synthesis of **ammonia** from its elements at 880° to 1000° and under 185 atm. press. The thermal decomposition of ammonia on osmium was studied by E. A. Arnold and R. E. Burk. J. J. Berzelius found that osmium is oxidized by conc. **nitric acid,** and L. N. Vauquelin dissolved it in **aqua regia.** J. J. Berzelius showed that osmium combines with the vapour of **phosphorus** with incandescence, forming a phosphide. W. Strecker and M. F. Schurigin found that **phosphorus pentachloride** or **phosphorus pentabromide** does not act on the spongy metal to form phosphohalides.

H. Moissan noted that molten osmium dissolves 3·89 to 3·97 per cent. of **carbon** and rejects it as graphite on cooling. H. Wölbling studied the adsorption of osmium by active carbon. J. Gerum, and C. Paal observed that **carbon monoxide** is oxidized by oxygen in the presence of osmium hydrosol at ordinary temp. K. A. Hofmann and O. Schneider found that the rate of oxidation of carbon monoxide with a soln. of sodium chlorate in the presence of a platinum metal decreased in the order Os, Rh, Au, Pt, Ru, Ir, Ag. F. Fischer and co-workers compared the activity of the platinum metals as catalysts in the reduction of carbon monoxide to methane. According to C. Paal, the hydrosol, and finely-divided osmium catalytically favour the oxidation of some **unsaturated organic** compounds —*e.g.* cyclohexane—and R. Willstätter and E. Sonnerfeld observed that this property is not shared under these conditions by the other platinum metals. J. E. Nyrop, and B. S. Srikantan studied the efficiency of osmium as a catalyst. N. D. Zelinsky and M. B. Turova-Pollak also found that it operates as a reducing agent for benzene, *cyclo*-hexadiene, *o*-xylene, *p*-xylene, mesitylene, indene, naphthalene, thujene, acetone, methylethylketone, *cyclo*-pentanone, and methyl *cyclo*-pentanone, at a lower temp. than platinum or palladium. R. Willstätter and E. Sonnerfeld studied osmium as a catalyst in the oxidation of *cyclo*-hexane; A. A. Balandin, its action in the dehydrogenation of decahydronaphthalene; C. Paal and J. Gerum, the hydrogenation of nitrobenzene; A. A. Balandin, the dehydrogenation of decahydronaphthalene. F. C. Phillips observed that osmium asbestos favours the oxidation of **ethylene,** and **trimethylene.** C. Paal and A. Schwarz studied the adsorption of **acetylene,** and found that the hydrogenation of acetylene is not affected by colloidal osmium. G. F. Hüttig and E. Weissberger

studied the catalytic decomposition of **methyl alcohol**; E. Müller, and E. Müller and co-workers, of **formic acid,** and of **formaldehyde.**

No compound of osmium with the metals is known. P. G. Ehrhardt observed that a **lithium-osmium alloy** is harder than osmium alone. J. O. Linde investigated the solubility of osmium in copper. S. Tennant prepared a **copper-osmium alloy** which is malleable and soluble in aqua regia; and W. Truthe studied the behaviour of the **osmium-silver alloy** on cupellation. S. Tennant prepared **gold-osmium alloy.** J. O. Linde discussed the solubility of osmium in gold. W. Truthe studied the behaviour of the alloy on cupellation. H. Debray, and H. St. C. Deville and H. Debray obtained a **zinc-osmium alloy** by dissolving osmium in molten zinc, and by extracting the zinc with an acid or by volatilization, crystals of osmium remain behind. S. Tennant, and J. J. Berzelius obtained **osmium amalgam,** or a **mercury-osmium alloy,** by the action of mercury on an aq. soln. of osmic acid. When the amalgam is heated, the mercury is expelled, and osmium remains as a black powder. H. St. C. Deville and H. Debray said that the amalgam wets glass, and containing vessels are rapidly "silvered." H. Debray said that the tin-osmium alloys gave no sign of the formation of a stannide. According to J. Stodart and M. Faraday, **iron-osmium alloys** can be prepared and the iron acquires a temper. The alloys were studied by R. A. Hadfield, P. Oberhoffer, and J. B. J. D. Boussingault. Treatment of the alloy with acids gives no evidence of any chemical compound. F. Wever studied the effect of osmium on the transformation points of iron. H. Remy and H. Gonnington studied the catalytic activity of the iron-osmium alloys; of the **cobalt-osmium alloys;** of the **nickel-osmium alloys;** of the **ruthenium-osmium alloys;** and of the **rhodium-osmium alloys.** F. E. Carter observed that owing to the difficulty in controlling the composition of the **palladium-osmium alloys,** they have not attracted much attention. An alloy with 25 per cent. of osmium has a Brinell's hardness of 200 when hard, and 100 when annealed; and an electric resistance of 120 ohms per million ft. They lose osmium when heated. H. Remy and H. Gonnington studied their catalytic activity.

F. Wöhler observed that when osmium is fused with **potassium hydroxide,** exposed to the air, potassium osmate is formed, and a similar result is obtained with potassium hydroxides and oxidizing agents, *e.g.* nitrate, chlorate, etc.—*vide supra,* opening osmiridium. E. Leidié and L. Quennessen obtained soluble sodium osmate by the action of molten **sodium dioxide.** E. Tiede and R. Piwonka studied the **alumina** osmium phosphors. J. J. Berzelius also observed that osmium is attacked by molten **alkali hydrosulphate.**

Some reactions of analytical interest.—When a soln. of osmium chloride in dil. nitric acid is distilled, and the vapours collected in a soln. of sodium hydroxide, alkali osmate is formed. If the yellow soln. be treated with acid, there is a penetrating odour characteristic of osmium tetroxide, and sodium thiosulphate produces a brown precipitate of osmium sulphide. A soln. of potassium chloro-osmate when treated with **hydrogen sulphide,** gives a dark brown precipitate of osmium sulphide, insoluble in ammonium sulphide; **potassium hydroxide** or **carbonate,** or aq. **ammonia,** give reddish-brown precipitates of hydrated oxide. A soln. of osmium tetroxide decolorizes **indigo-blue;** and, according to E. P. Alvarez,[3] it forms green osmium hydriodide when treated with an acidic soln. of **potassium iodide**—in the presence of phosphoric acid and ether, the reaction is sensitive to 1 in 200,000 of osmium tetroxide in soln. In the presence of ether, a few millionths of a gram of osmium can be recognized by the green colour of the ethereal layer. A soln. of osmium tetroxide oxidizes **alcohol** to aldehyde and acetic acid and the soln. becomes dark blue; a similar coloration is produced with **tannic acid.** When the soln. of osmium chloro-osmate is treated with **potassium nitrite,** garnet-red crystals are developed; with **sulphurous acid,** the sequence of colour changes: yellow, reddish-brown, green, and indigo-blue is developed; **ferrous sulphate** precipitates black osmium dioxide; **stannous chloride** gives a brown precipitate soluble in hydrochloric acid; and **zinc** and several other metals in the presence of free acid

precipitate metallic osmium. The soln. are also reduced to metal by **sodium formate,** and, according to H. Erdmann, and O. Makowka, by **acetylene.** V. N. Ivanoff said that **thiocyanates** do not give definite precipitates with soln. of osmium salts ; but M. Hirsch said that the blue colour developed when the mixture is shaken with ether or amyl alcohol is just perceptible in a dilution of 1 part of osmium per million parts of soln. On warming a soln. of potassium osmate with **aniline sulphate** a deep rose coloration appears; potassium chloro-osmate gives a violet one ; and **β-naphthylamine hydrochloride, pyrocatechol,** or **pyrogallol** gives a deep blue (S. C. Ogburn). Osmium salts also give precipitates with **strychnine sulphate** (S. C. Ogburn and L. F. Miller). V. G. Chlopin observed that **benzidine** with salts of quadrivalent osmium gives a yellow precipitate and with perosmic acid, a blue colour; and L. Wöhler and L. Metz, a red colour with **thiocarbanilide.** E. Müller studied the reduction of **formaldehyde** with osmium as catalyst. L. A. Tschugaeff, when a soln. containing osmium in the form of its tetroxide or as a chlorosmate is warmed for a few minutes with **thiocarbamide,** in excess, and a few drops of hydrochloric acid, the liquid acquires a deep red or a rose colour, according to the conc. of the osmium. By this means, osmium may be detected at a dilution of 1 in 100,000. W. Singleton recommended the reactions with potassium thiocyanate and ether, or amyl alcohol ; and with thiocarbamide in hydrochloric acid soln.

Physiological action.—J. J. Berzelius [4] said that air containing osmium tetroxide attacks the lungs strongly when inhaled, producing long-continued expectoration, and it also excites a burning sensation in the eyes. L. N. Vauquelin said that when respired it imparts *un sentiment douloureux.* F. Wöhler added that extremely small quantities of the vapour act violently on the eyes and lungs. C. G. Gmelin said that osmium salts acting on the stomach quickly cause vomiting, and in the vascular system, it causes a very copious discharge of a serous fluid from the lungs, thus effecting a stoppage in the pulmonary circulation. When injected into the stomach of a rabbit, vomiting occurred, the rabbit then refused to eat, became emaciated, and recovered slowly. Another injection resulted in a paralysis of the extremities, followed by death. The surface of the œsophagus, stomach and small intestines was bluish-black, interior was as black as charcoal, and hard. The small intestines showed no change. The wall of stomach in the vicinity of the cardiac orifice was œdematous. The heart, lungs, liver, spleen, bladder, kidney, and nerves were in natural state. The black colour is due to reduction of osmium by animal matter. No trace of inflammation was perceptible upon the blackened parts, they had not a bad smell, and could not be torn with more ease than in the natural state. F. R. Brunot found that animals breathing the fumes of osmium tetroxide in high concentration develop pneumonia, and die. According to R. Seeliger, wheat corn withstands for some hours, without being killed, relatively high concentrations of osmium tetroxide, although in lower concentrations this oxide retards germination, delays growth, and results in diminution of the magnitude of the organs of the young plant. The parenchymatous cells of the red beet are highly sensitive to the action of osmium tetroxide. According to E. Wichers and co-workers, in working with osmium, consideration must always be given to the danger of poisoning from osmium tetroxide. Even in minute quantities the vapours are very irritating to the mucous membranes. Prolonged exposure to small concentrations, as well as brief contact with larger amounts, may cause serious and possibly permanent injury, especially to the eyes. Fortunately, the compound has a penetrating, readily recognizable odour, which serves as a warning. The poisonous vapours, said H. St. C. Deville and H. Debray, produce temporary blindness and other unpleasant symptoms. C. Claus recommended the immediate inhalation of hydrogen sulphide as an antidote for neutralizing the action of the tetroxide on the respiratory organs. Observations on the physiological action were made by F. Brauell, A. Butleroff, G. M. Holse, P. Owsjannikoff, A. F. Coca, F. Rosenthal, and A. von Szily—*vide infra*, the uses of osmium.

Some uses of osmium.—Osmium is employed in the form of osmiridium, and in some synthetic alloys for pen-point material, and for sparking points. Osmium has been used in the manufacture of the filaments of incandescent lamps, by A. von Auerbach.[5] S. Tennant, and L. N. Vauquelin observed that a soln. of osmium tetroxide—called osmic acid—blackens organic substances, even the cuticle, especially when they are wet, by reduction to what they assumed to be metallic osmium. Soln. of perosmic acid, (OsO_4), "osmic acid," are also used in differentiating tissues under the microscope—M. Shultze, L. A. Ranvier, R. Palmer, L. Golodetz, and J. R. Partington and D. B. Huntingford studied the nature of the black stain produced by fats and allied substances, and concluded that it is a hydrated osmium dioxide.

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§ 5. The Atomic Weight and Valency of Osmium

The at. wt. of osmium is about 190·9. The element is *bivalent* in the monoxide and dichloride ; and *tervalent* in the sesquioxide and trichloride where it forms salts, $2NH_4Cl.OsCl_3$, analogous with corresponding salts of ruthenium trichloride, and ferric chloride. Osmium is *quadrivalent* in the dioxide, tetrafluoride, and tetrachloride, and the double salts, $2KCl.OsCl_4$, analogous with the isomorphous $2KCl.RuCl_4$, and with $2KF.MnF_4$. The element is *sexivalent* in the hexafluoride, OsF_6, and in the osmates, K_2OsO_4, analogous with the corresponding ruthenates, ferrates, manganates, and sulphates. Osmium behaves like an *octovalent* element in the tetroxide, OsO_4, which is analogous with ruthenium tetroxide. E. Ogawa [1] studied the constitution of the tetroxide. He said :

There are two different theories on the constitution of osmium tetroxide. S. Sugden says that it must be a semi-polar compound, while N. V. Sidgwick regarded it as a co-valent compound. N. V. Sidgwick said that, according to his valency theory, since the elements of first sub-group or VIIIth group, iron, ruthenium, and osmium, have eight electrons more than an inert gas, they might be expected to show the valency of eight, especially in 8-covalent compounds which could be formed directly without co-ordination. But by the covalency rule, the maximum covalency of an atom is 2 for hydrogen, 4 for the elements from lithium to fluorine, 6 for the elements from potassium to bromine, and 8 for the elements from rubidium to uranium. So the elements which can form 8-covalent compounds directly without co-ordination are ruthenium and osmium only. Osmium octofluoride, OsF_8, is an illustration of a compound of octovalent osmium ; and it is at least probable that osmium tetroxide, OsO_4, has a similar 8-covalent structure :

$$\begin{matrix}O\\O\end{matrix}\!\gg\!Os\!\ll\!\begin{matrix}O\\O\end{matrix} \quad \text{and not} \quad \begin{matrix}O\nwarrow\\O\swarrow\end{matrix}\!>\!Os\!<\!\begin{matrix}\nearrow O\\\searrow O\end{matrix}$$

This is supported by the fact that ruthenium, which also can be 8-covalent, likewise forms a volatile tetroxide ; but iron, which is limited to a covalency of six, does not. R. C. Menzies studied the co-ordination number of osmium.

The measurement of parachor by S. Sugden, and the isolation of the compounds by F. Krauss, indicate that osmium tetroxide must be an unsaturated co-ordination compound, and E. Ogawa said that these facts are strong objections

to the covalency theory. S. Sugden calculated 154·0 for the parachor of osmium tetroxide using the data measured by H. von Wartenberg. Assuming that the osmium has an octet, there must be four semi-polar links (or co-ordinate links according to N. V. Sidgwick) in the molecule; and the parachor for osmium will be: $Os=154{\cdot}0-4\times20{\cdot}0+4\times1{\cdot}6=80{\cdot}4$. On the other hand, if the molecule is analogous to the octofluoride, OsF_8, and has four true double links, the parachor, according to S. Sugden's values, should be $Os=154{\cdot}0-80{\cdot}0-4\times23{\cdot}2=-18{\cdot}8$. S. Sugden said that there is no other evidence of the value of the parachor of osmium, but from rough data for the neighbouring elements it should be between 60 and 100. Hence, he concluded that the formula is to be represented by:

$$\begin{matrix} O\nwarrow & & \nearrow O \\ & Os & \\ O\swarrow & & \searrow O \end{matrix}$$

According to N. V. Sidgwick, S. Sugden's argument may seem at first sight to be conclusive, but there are some difficulties. In the first place, the close agreement between theory and observation which he obtained with the other substances cannot be adduced here, because of the lack of data as to the parachor of osmium. Secondly, in all the substances for which the agreement was found to be close, there is the evidence of the presence (in every atom except hydrogen) of an octet. Hence, added N. V. Sidgwick, there is no proof that S. Sugden's values hold good when the valency group exceeds eight; this might be expected to affect the mol. vol., and that, in addition to the constitutive factors of the parachor, another factor would be needed to allow for the change in size of the valency group. This would presumably be negative; the high stability and screening effect of the octet as compared with any other arrangement of the outer electrons suggest that when there is a larger valency group the external field is stronger, and the attached atoms are more closely held together. For example, in zinc, where the group next to the valency electrons is eighteen, the vol. is much smaller than in calcium, where it is eight. In osmium tetroxide, if the metal is really 8-covalent, there is an extreme case of this effect, since the valency group has expanded from eight to sixteen, and it may be concluded that if this occurred, it would considerably reduce the parachor, so that the fact that such a formula would give a negative value for the parachor of osmium, when no allowance is made for the change in the valency group, is not conclusive evidence that the formula is wrong.

In support of S. Sugden's theory, F. Krauss and D. Wilken reported the isolation of some compounds of the types: $Cs_2[OsO_4(OH)_2]$, and $Cs_2[OsO_4F_2]$, which indicate that osmium tetroxide is an unsaturated co-ordination compound. This fact is an objection to N. V. Sidgwick's theory. In short, added E. Ogawa, this question is not yet solved.

In support of an at. wt. of the order 191 for osmium, the vap. density determinations of osmium tetroxide show that the at. wt. is either 191 or a submultiple of this value. The at. wt., 191, is in accord with the sp. ht. rule, and with the isomorphous rule exemplified by the chloro-osmates, K_2OsCl_6, and the corresponding compounds of palladium, iridium, and platinum; the isomorphism of potassium osmocyanide, ruthenocyanide, and ferrocyanide; and the examples cited above. M. Gerber studied some relations of the at. wts. The relations of osmium to the other elements were discussed by J. W. Mallet,[2] who considered it belonged to the arsenic family on the assumption that its at. wt. is half the value now accepted. The value 191 is in accord with the position of osmium in the periodic table where its close and unique relations with ruthenium are emphasized, and an at. wt. between the values 186·31 for rhenium, and 193·1 for iridium.

In 1828, J. J. Berzelius analyzed potassium chloro-osmate, and from the ratio 2KCl : Os, calculated the at. wt. to be 198·9; and in 1844, E. Frémy obtained 199·7 from an analysis of the tetroxide. Both these values are not in accord with the natural position of osmium in the periodic table, and consequently, in 1888, and in 1891, K. Seubert re-determined this constant, and obtained 191·25 from the

ratio $(NH_4)_2OsCl_6 : Os$; 192·23 from the ratio $6AgCl : (NH_4)_2OsCl_6$; 190·27, and 191·14 from the ratio $K_2OsCl_6 : 2KCl$; 191·23 from the ratio $6AgCl : K_2OsCl_6$; and 190·38 from the ratio $K_2OsCl_6 : Os$. F. Seybold calculated 189·4, and 191·1 from the ratio $(NH_4)_2OsCl_6 : Os$; and R. Gilchrist, 191·53 from the ratio $(NH_4)_2OsCl_6 : Os$, and 191·58 from the ratio $(NH_4)_2OsBr_6 : Os$. F. W. Clarke calculated 191·067 for the best representative value ; and the International Table for 1935 gave 190·9.

The **atomic number** of osmium is 76. According to F. W. Aston,[3] there are six **isotopes** with atomic weights, relative abundances, and percentage abundances as follow :

Mass numbers . .	186	187	188	189	190	192
Abundance relative .	2·4	1·4	31·6	40·8	58·9	100
Abundance percentage .	1·0	0·6	13·5	17·3	25·1	42·6

in accord with the mean mass number 190·35, which, when corrected to the chemical scale gives an at. wt. of 190·31 which is smaller than the value 190·9 indicated above. Neither E. Rutherford and J. Chadwick, nor H. Petterssen and G. Kirsch, have observed the **atomic disruption** of osmium by the bombardment with α-rays. The **electronic structure,** according to N. Bohr, and E. C. Stoner, is (2) for the K-shell ; (2, 2, 4) for the L-shell ; (2, 2, 4, 4, 6) for the M-shell ; (2, 2, 4, 4, 6, 6, 8) for the N-shell ; (2, 2, 4, 4, 2) for the O-shell ; and (2) for the P-shell—or else (2, 2, 4, 4, 3) for the O-shell, and (1) for the P-shell. The subject was studied by P. D. Foote, W. Hume-Rothery, S. Kato, H. G. Grimm, S. K. Allison, G. I. Pokrowsky, H. J. Walke, and C. D. Niven.

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§ 6. The Osmium Oxides

J. J. Berzelius[1] treated a soln. of the double salt of potassium chloride and osmium dichloride with potash lye, and in a few hours obtained a greenish-black precipitate of **osmium dihydroxide,** possibly $Os(OH)_2$, or **hydrated osmium monoxide.** It retains the alkali very tenaciously. C. Claus said that the product is very impure ; and C. Claus and E. Jacoby, and E. Jacoby obtained the hydrate by warming osmium sulphite with a conc. soln. of potassium hydroxide in an atm. of inert gas. The bluish-black precipitate is rapidly washed with hot water ; it is rapidly oxidized on exposure to air. According to J. J. Berzelius, when the hydrate is heated with combustible substances, it detonates forming osmium ;

with hydrogen at ordinary temp., heat is generated, and water and osmium are formed; and when ignited to incipient redness, in closed vessels, water is given off, but no osmic acid is evolved, and **osmium monoxide,** OsO, is formed. This oxide was obtained by C. Claus by heating a mixture of sodium carbonate with potassium osmium sulphite, or, according to C. Claus and E. Jacoby, osmous sulphite, in a current of carbon dioxide, and washing the product with water. The greyish-black powder is insoluble in acids. According to E. Frémy, and O. W. Gibbs, when ammonia acts on potassium osmate, a brown liquid is formed which is supposed to contain **osmium diamminodihydroxide,** $[Os(NH_3)_2](OH)_2$, or $[Os(NH_3)_2(OH)_2]$.

According to C. Claus and E. Jacoby, **hydrated osmium hemitrioxide,** $Os_2O_3.nH_2O$, is produced as a reddish-brown precipitate when an alkali is added to an aq. soln. of potassium chlorosmite; and **osmium hemitrioxide,** Os_2O_3, or **osmium sesquioxide,** is formed as a black powder when salts of tervalent osmium are heated with sodium carbonate in a current of carbon dioxide, and washed with water. H. St. C. Deville and H. Debray prepared it in copper-red scales by heating osmium tetroxide with finely-divided osmium. The product is insoluble in acids.

J. J. Berzelius referred to a *blue oxide of osmium* which was supposed to be a mixture of the monoxide and sesquioxide, or of the monoxide and dioxide, and he obtained it as a blue coloration by the action of sulphurous acid on an aq. soln. of osmic acid; S. Tennant obtained it by the action of tincture of galls on a soln. of osmic acid; and H. V. Collet-Descotils, and L. N. Vauquelin, as the first film of sublimate of oxide formed when osmium or osmiferous platinum is heated in a retort containing air.

According to J. J. Berzelius, E. Jacoby, and C. Claus and E. Jacoby, when salts of quadrivalent osmium are heated with sodium carbonate in a current of carbon dioxide, and extracted with water and hydrochloric acid, there is formed **osmium dioxide,** OsO_2; if air be present, volatile osmium tetroxide may be formed. The same compound is produced when one of the dried hydrates is heated in an atm. of nitrogen, or carbon dioxide, a small quantity of volatile osmium tetroxide may be formed, and some hydrogen given off: $2Os(OH)_4=OsO_4+OsO_2+2H_2O+2H_2$. H. Rathsburg, and O. Ruff and H. Rathsburg obtained the dioxide by heating very finely-divided osmium in an atm. of nitrogen and the vapour of osmium tetroxide at 650°. H. Moraht and C. Wischin obtained the dioxide by electrolyzing a soln. of potassium perosmate; and A. Joly, by heating potassium osmiamate, $KOsNO_3$, in vacuo, at 350°. H. Freundlich and F. Oppenheimer prepared the colloidal oxide.

The dioxide may appear as a black, or greyish-black powder, or in copper-red, octahedral or hexahedral crystals, which, according to V. M. Goldschmidt, are tetragonal with $a=4\cdot51$ A., $c=3\cdot19$ A., and $a:c=1:0\cdot707$. G. Lunde studied the subject. The amorphous, bluish-black dioxide obtained by dehydrating the dihydrate at 200° was found by O. Ruff and H. Rathsburg to have a sp. gr. of 7·71; and when further heated to 400°, they noted that the colour changes to dark brown, and the sp. gr. increases slightly. At about 460°, the dioxide begins to decompose into osmium, and osmium tetroxide, but the reaction: $2OsO_2 \rightleftharpoons 2Os+2O_2$, right to left, is favoured in the vapour of osmium tetroxide, and the copper-red crystals of the dioxide thus formed at 650° have a sp. gr. of 7·91 at 21. F. Krauss and G. Schrader, and G. Schrader obtained for the sp. gr. 11·375 at 21°/4°; F. Wöhler, V. M. Goldschmidt, and F. Krauss and G. Schrader gave 19·6 for the mol. vol., and O. Ruff and H. Rathsburg, 28·2 to 29·0. J. J. Berzelius found that the dioxide can be heated to near redness out of contact with air without decomposition; it is reduced by hydrogen at ordinary temp.; it detonates when heated with combustible substances; and it is insoluble in acids. According to O. Ruff and H. Rathsburg, the dioxide prepared by the reduction or hydrolysis processes retains alkali and organic substances very tenaciously, and the dry powder is *pyrophoric osmium dioxide.* It is more or less dangerous to handle, as it may

kindle on exposure to the air or detonate on warming. An old preparation, or one that has been warmed with water for some time with a view to its purification, will not be so dangerous, but then it will contain much free metallic osmium. The determination of osmium as dioxide, as recommended by O. Ruff and F. Bornemann, is therefore untrustworthy.

H. Freundlich and H. Baerwind prepared a *colloidal solution* of osmium dioxide by shaking the hydrated dioxide with water. The colloidal particles are negatively charged and migrate to the anode. The sol, in its behaviour to electrolytes, shows the behaviour typical of negatively charged sols, that is, the kation of the precipitating electrolyte is determinative of the action of the electrolyte. The precipitation values are in keeping with the valency rule. The particles are not spherical. The addition of gelatin to osmium dioxide sols at first brings about coagulation which is followed by a protective action. In keeping with this, the addition of gelatin to the electrolytes exercises both a sensitizing and a protective action. The sol is not coagulated at any concentrations by tannin and saponin. The migration velocity of osmium dioxide sols on the addition of gelatin increases almost up to the coagulating concentration; it then falls and finally increases, but there is no reversal of the charge of the sol. The osmium dioxide sol, as such, has no decomposing action on formic acid at 100°, but it is reduced to the metal sol, and this brings about a rapid decomposition of the acid. C. Amberger prepared the colloid by using lanolin as protective colloid when a soln. of potassium osmate is treated with hydrazine hydrate. S. Medvedeff and E. Alexeeva studied the dioxide as a catalyst in the oxidation of unsaturated hydrocarbons.

C. Claus reported a *pentahydrate*, $OsO_2.5H_2O$, to be formed, in an impure state, by the action of ammonia on a chloro-osmate; it is inclined to form an ammine in the presence of ammonia. E. Frémy obtained the *monohydrate*, $OsO_2.H_2O$, or $OsO(OH)_2$, as a black powder, by heating the dihydrate at 120° to 130° in an inert gas; J. J. Berzelius, and O. Ruff and H. Rathsburg, prepared the *dihydrate*, $OsO_2.2H_2O$, or **osmium tetrahydroxide,** $Os(OH)_4$, by treating a conc. soln. of potassium chlorosmate by an alkali carbonate or hydroxide: $K_2OsCl_6+4KOH=6KCl+OsO_2.2H_2O$, and it is difficult to remove the last traces of alkali chloride from the product. A. Butleroff obtained the dihydrate by the action of alcohol on an alkali osmate, $K_2OsO_4+2H_2O+C_2H_5OH=CH_3.COH+2KOH+OsO_2.2H_2O$; and C. Claus, by the action of dil. nitric acid, and E. Frémy, by the action of dil. sulphuric acid on a soln. of potassium osmate. The dihydrate appears as a bluish-black, amorphous powder which is very voluminous, and becomes dark brown when dried. C. Claus, E. Jacoby, and C. Claus and E. Jacoby observed that when heated it is liable to detonate and form the dioxide, tetroxide, water, and hydrogen. For O. Ruff and H. Rathsburg's observations on the action of heat, *vide supra;* when the dioxide is obtained from the hydrate, a copper-red sublimate is usually deposited on the tube—possibly osmium tetroxide—and it may be that the hydrate passes into the trioxide, OsO_3, which decomposes $2OsO_3 \rightleftharpoons OsO_2+OsO_4$. C. Claus and E. Jacoby said that the moist hydrate dissolves freely in hydrochloric acid, whilst the dried hydrate dissolves sparingly in that acid. Some oxidation occurs when the hydrate is dissolved in nitric and sulphuric acids. According to F. Wöhler, the soln. in conc. hydrochloric acid is at first purple, it then becomes yellowish-brown, and lastly green—or if heated brownish-yellow; sulphurous acid colours it yellow, and nothing is deposited when the soln. is boiled. E. Frémy said that ammonium chloride colours the soln. in acids yellow.

According to C. Claus, and J. J. Berzelius, if osmium tetroxide is treated with an excess of conc. aq. ammonia, and the yellow liquid heated in a closed vessel at 50° until it becomes dark brown in colour and a black powder is deposited, and then exposed to the atmosphere, a blackish-brown powder of **osmium oxydiamminodihydroxide,** $[OsO(NH_3)_2](OH)_2$, is formed when the liquid is evaporated at a low temp. The product decomposes explosively when heated with the evolution of

nitrogen ; it dissolves in acids yielding the corresponding salts ; and the base can be reprecipitated from the soln. in acids by the addition of alkali hydroxide, but boiling the base with alkali lye decomposes it with the liberation of ammonia, and the deposition of osmium dioxide. W. Eichler prepared what he regarded as a **potassium perosmite,** $K_2O.3OsO_2$, by exposing an aq. soln. of potassium osmate to sunlight. The liquid becomes turbid and deposits a sooty black powder. It is soluble in cold, conc. hydrochloric acid, forming a soln. of chloro-osmate. Aq. ammonia, and potash lye precipitate black hydrated osmium dioxide from the soln. In contact with air, the soln. gives off vapours of osmium tetroxide.

O. Ruff and H. Rathsburg prepared **colloidal osmium dioxide** by reducing soln. of alkali osmates with alcohol, or by the hydrolysis of chlorosmates—*vide supra.* The dioxide is again precipitated on adding sufficient electrolyte to the neutral soln., but it forms a colloidal soln. again when treated with acids, alkali hydroxides, or ammonia or washed free from electrolytes. Conc. soln. appear black by reflected light or blue by transmitted light. A permanent hydrosol was obtained by C. Amberger by using lanolin as a protective colloid when a soln. of potassium osmate is reduced with hydrazine hydrate. The product can be dissolved in light petroleum, and the soln. is precipitated by alcohol. When the precipitate is heated to 50° in hydrogen, the colloidal dioxide is reduced to osmium.

J. W. Mallet fused some platinum residues with nitre, and warmed the product with sulphuric acid and obtained yellow drops as a sublimate, and they congealed to a yellow wax ; farther away, osmium tetroxide appeared in colourless needles. When the yellow solid, in a sealed tube, was exposed to solar rays, needles and prisms resembling osmium tetroxide appeared as a sublimate, and the yellow mass became black in colour. J. W. Mallet thought that the yellow product is impure **osmium trioxide,** OsO_3, which breaks down into osmium tetroxide and a lower oxide or osmium itself. The yellow product was more likely to have been an impure dioxide. H. Moraht and C. Wischin obtained a black substance by the action of heat on a mixture of potassium osmate and nitric acid. It was first obtained by W. Eichler, afterwards by E. Frémy, and then by C. Claus and E. Jacoby, by exposing a soln. of potassium osmate to sunlight ; they assigned to it the formula $OsO_3.2H_2O$, but H. Moraht and C. Wischin found that when dried over phosphorus pentoxide, in vacuo, its composition corresponds with the hydrate, $OsO_3.H_2O$, or **osmic acid,** H_2OsO_4. O. Ruff and K. Bornemann could not confirm the analysis, and considered the product to be the hydrated dioxide. H. Moraht and C. Wischin report that osmic acid is sooty-black, and when dry does not possess the coppery lustre characteristic of the dihydrated dioxide. In moist air, it has the odour of osmium tetroxide ; it is stable under water containing alcohol, it dissolves in hydrofluoric acid ; with hydrochloric acid it forms an olive-green soln. smelling of chlorine, and when the soln. is evaporated, it yields crystals of $Os_2Cl_7.7H_2O$—probably a mixture of chlorides ; hydrobromic acid reacts like hydrochloric acid, forming crystals of $Os_2Br_9.6H_2O$—probably a mixture of bromides ; iodine vapour has no action ; hydriodic acid reacts, forming osmium tetraiodide ; it is not attacked by sulphuric acid ; hydrogen sulphide reacts violently producing an oxysulphide ; bromine vapour has no action ; it dissolves in nitric acid to form osmium tetroxide.

L. Wintrebert found that the bivalent radicle, which he called **osmyl,** OsO_2, persists through a series of compounds, and in this respect resembles the radicle uranyl, UO_2. Hence osmium trioxide can be regarded as osmyl oxide, $(OsO_2)O$, and osmic acid, as **osmyl hydroxide,** $OsO_2(HO)_2$. The chloride, sulphite, nitrite, oxalate, etc., form complex salts typified by $2KCl.(OsO_2)Cl_2$, or $K_2(OsO_2)Cl_4$; ammino-salts have also been obtained. L. Wintrebert also obtained **osmyl oxysalts** in which the group $(OsO_2)O$ unites additively with various salts—chlorides, bromides, and nitrites. When osmyl tetramminochloride is treated with moist silver oxide, or osmyl tetramminosulphate is treated with barium hydroxide, a strongly alkaline, yellow liquid is formed which readily absorbs carbon dioxide

from the atmosphere; the liquid contains **osmyl tetramminohydroxide,** $[OsO_2(NH_3)_4](OH)_2$, although all attempts to isolate the base have been nugatory because on concentration, the soln. decomposes into osmium tetroxide and ammonia.

E. Frémy obtained **potassium osmate,** $K_2OsO_4.2H_2O$, by reducing an alkaline soln. of osmium tetroxide with alcohol; E. Frémy, O. W. Gibbs, and C. Claus used potassium nitrite, as reducing agent; E. Frémy, and C. Claus obtained it by simply boiling an alkaline soln. of osmium tetroxide—it is thought that the reduction is here produced by impurities in the alkali; and E. Frémy obtained it from a soln. of osmium dioxide in an alkaline soln. of osmium tetroxide. O. Ruff and K. Bornemann obtained the salt by fusing osmium with a mixture of potassium hydroxide and nitrate, dissolving the product in water, precipitating with alcohol, and oxidizing the product with chromic acid in a current of oxygen. The osmium tetroxide so formed is passed into a 10 per cent. soln. of potassium hydroxide, the salt precipitated by alcohol, and dried in vacuo. The salt is deposited from the conc. aq. soln.; with slow evaporation, rose-red, garnet-red, violet, or black crystals; and H. Behrens said that the violet octahedra belong to the rhombic system. According to H. Moraht and C. Wischin, the salt can be kept in the cold exposed to sunlight for many days with very little decomposition. E. Frémy, and C. Claus found that the crystals do not lose water at 100°; but they lose their water of crystallization at 200° in an inert atm. When the salt is warmed decomposition is accelerated, and the odour of osmium tetroxide appears. When heated in inert atm., alkali hydroxide, osmium dioxide, and osmium tetroxide are formed. According to E. Frémy, and C. Claus, hydrogen reduces the salt to osmium and potassium hydroxide. The salt is stable in dry air, and when heated in air, it first loses water, then absorbs oxygen and forms volatile osmium tetroxide, and potassium perosmate; and even if heated in oxygen, not all the osmium is converted into the tetroxide. The salt is rapidly decomposed in moist air and develops osmium tetroxide; cold water dissolves a little of the salt, and the soln. acquires the colour of a permanganate, reacts alkaline, gradually becomes turbid with the separation of hydrated osmium dioxide, whilst osmium tetroxide remains in soln. Hot water freely dissolves the salt with decomposition. The decomposition is favoured by acids, and retarded by alkali. Chlorine transforms the salt into a perosmate; hydrogen sulphide forms osmium sulphide; sulphurous acid acquires a blue colour, and osmium sulphide or potassium osmium sulphite is formed; aq. ammonia dissolves the salt forming an ammine; a soln. of ammonium chloride forms ammonium osmyl chloride, $(NH_4)_2(OsO_2)Cl_4$. Organic substances reduce the salt forming osmium; it is not dissolved by alcohol or ether. Carbonic acid hastens the decomposition of the aq. soln., and when the salt is heated in carbon dioxide, alkali carbonate, and osmium dioxide and tetroxide are formed. Hydrochlorides of cinchonine, narcotine, and other alkaloids behave like ammonium chloride in forming a complex salt. In the presence of an excess of hydrochloric acid, gold, or platinum chloride produces a crystalline double salt; palladium chloride produces a yellowish-brown soln. from which hydrochloric acid precipitates a complex salt. Cobaltic hexamminochloride or sulphite was found by O. W. Gibbs to give a brownish-yellow precipitate containing osmium and cobalt, which forms a wine-yellow soln. with hydrochloric acid, and which gives crystalline double salts with mercury, gold, and platinum chlorides. M. C. Lea found that an ammoniacal soln. of sodium antimony sulphide gives a brown precipitate with a soln. of potassium osmate.

E. Frémy also prepared **sodium osmate,** $Na_2OsO_4.nH_2O$, which crystallizes with difficulty; it is soluble in water, and is insoluble in alcohol and ether; when the aq. soln. is treated with barium chloride, there is formed a green, flocculent precipitate of **barium osmate,** $BaOsO_4.nH_2O$, which changes into black, lustrous prisms; similarly with **strontium osmate,** $SrOsO_4.nH_2O$; **calcium osmate,** $CaOsO_4.nH_2O$; and **lead osmate,** $PbOsO_4.nH_2O$.

As indicated in connection with the chemical properties of osmium, J. J. Ber-

zelius observed no oxidation of osmium by air occurs in the cold or at 100°, although the smell of osmium at ordinary temp., according to H. Rose, and H. St. C. Deville and H. Debray, shows that a volatile oxide is being formed, and the metal also darkens the walls of the containing vessel. Finely-divided osmium at ordinary temp. was observed by H. St. C. Deville and H. Debray to form **osmium tetroxide,** OsO_4. The finely-divided osmium inflames in air at 400°, and produces this volatile tetroxide, which is sometimes called **osmic acid,** particularly when in aq. soln. To avoid confusion with osmic acid, H_2OsO_4, the aq. soln. of the tetroxide can be called **perosmic acid,** and the tetroxide thus becomes *perosmic anhydride.* J. J. Berzelius prepared osmium tetroxide by passing oxygen over osmium heated to redness in the first of two bulbs on a hard glass tube; the second bulb is kept cool. All but about 2 or 3 per cent. of the tetroxide collects in the second bulb, and the gas which passes on is led through aq. ammonia or potash-lye. The lower oxides of osmium also pass into the volatile tetroxide when they are heated in air; and the oxide is formed when osmium is heated with potassium hydroxide in air, or with a mixture of potassium hydroxide and nitrate. W. H. Wollaston heated osmiridium with nitre, dissolved the cold product in water, added dil. sulphuric acid (1 : 1), and distilled off the osmium tetroxide. J. J. Berzelius, and F. Wöhler obtained the tetroxide by heating the lower osmium oxides, the chloride, or the chloro-osmates with nitric acid; J. J. Berzelius, by passing chlorine mixed with the vapour of osmium chloride, into milk of lime; C. Claus, by passing chlorine into potash lye with finely-divided hydrated osmium dioxide in suspension; A. Butleroff, J. J. Berzelius, C. Claus, C. Claus and E. Jacoby, E. Frémy, A. Laugier, and H. Moraht and C. Wischin, by decomposing potassium osmate with dil. acids, or by boiling an aq. soln. of this salt whereby potassium hydroxide is liberated, and osmium tetroxide is volatilized; and F. Wöhler, by the electrolysis of potash lye with porous osmium as the anode.

L. N. Vauquelin said that osmium tetroxide furnishes colourless, transparent, acicular crystals which, according to J. W. Mallet, belong to the monoclinic system. P. Niggli and W. Nowacki discussed the crystal structure. H. St. C. Deville and H. Debray found that the **vapour density** is 8·89 (air unity) or 128 (hydrogen unity) when the theoretical value for OsO_4 is 127·5. The vapour thus contains OsO_4 mols. F. Krauss and D. Wilken studied the constitution of the tetroxide—*vide supra,* valency of osmium. H. von Wartenberg found the **specific gravity** to be 4·44 and 4·19, respectively, at 42° and 100°; and 4·91 at 22°. G. Schrader, and F. Krauss and G. Schrader gave 4·959 for the sp. gr. at 21°/4°, and 51·4 for the **molecular volume.** E. Ogawa found that the densities of the liquid, D, and of the vapour, d, are:

	43°	58°	75°	95°	115°	150°
D	4·3224	4·2620	4·1923	4·1108	4·0271	3·8733
d	0·0006	0·0010	0·0015	0·0027	0·0048	0·0131
Parachor . .	156·2	156·8	157·5	157·6	157·9	158·4

S. Sugden's value for the **parachor** from H. von Wartenberg's data is 154·0; the mean of all E. Ogawa's data is 157·7. The results above 75° correspond with $D-d=D_0(1-T_c)^{0\cdot3}$, when D_0 is the density at absolute zero, and T_c is the reduced critical temp. in °K. The results show that the tetroxide is a normal liquid above 75°, and that the molecules are partly associated at temp. below 75°. H. von Wartenberg gave 49·8 and 42·2 for the **surface tension,** σ dynes per cm., of the liquid tetroxide at 50·0° and 100·0°, respectively. E. Ogawa gave:

	43°	58°	75°	95°	115°	150°
σ	49·24	47·25	45·03	41·62	38·59	33·32

and the results can be represented by $\sigma=\sigma_0(1-T_c)^{1\cdot2}$. The whole of the results furnish two straight lines intersecting at about 75°. The **specific cohesion** at the b.p. is $a^2=1\cdot867$.

H. von Wartenberg gave 0·00102 for the coeff. of **thermal expansion.** L. N. Vauquelin said that osmium tetroxide readily fuses; L. F. Svanberg said that fusion occurs even by heat from the hand, and he gave 40° for the **melting point**; F. W. Tschirch, and O. Ruff and F. W. Tschirch, 45°; H. von Wartenberg, 40·1°; and E. Ogawa, 40·6° to 40·7°.

F. Krauss and D. Wilkin inferred that osmium tetroxide furnishes enantiotropic isomers, one, white, melting at 39·5°, and the other, yellow, melting at 41·0°. The white crystals melt to form a yellow transparent liquid which solidifies to a light yellow, or white opaque mass which, when heated again, melts at 41·0°. E. Ogawa said that the white needles do not melt at 39·5°, but at 40·6° to 40·7°, and the solidified light yellow mass has the same m.p. F. Wöhler observed that the tetroxide boils and evaporates at a moderate heat. A slight rise of temp. causes it to sublime in needles from one part to the other of the vessel in which it is kept. H. St. C. Deville and H. Debray said that when fused, it boils without decomposition near 100°. F. Krauss and D. Wilkin gave 134° for the **boiling point**; E. Ogawa, 131·2°; O. Ruff and F. W. Tschirsch, 130°; and H. von Wartenberg, 129°. F. Krauss and D. Wilkin said that the yellow form changes into the white in liquid air, and it then becomes breakable with a glass rod, and melts at 39·5°. E. Ogawa found that the yellow form did not change its colour when left in liquid air for 24 hrs., and its m.p. remained 40·6°. F. Krauss found that the **vapour pressure,** p mm., of the white and yellow forms are different:

	White form					Yellow form				
	0°	10°	18°	29°	36°	0°	12°	18°	28°	35°
p . . .	2·0	3·5	5·0	7·0	9·0	0·5	2·0	3·0	5·0	7·5

Both forms have the same vap. press. at 41·0°. H. von Wartenberg said that the vapour is stable up to 1500°. Measurements of the vap. press. of the tetroxide have been made by F. W. Tschirch, and O. Ruff and F. W. Tschirch. H. von Wartenberg's results for the liquid and solid are:

	Solid			Liquid				
	−38·0°	−19·6°	0°	40·2°	51·0°	67·8°	91·0°	136·4°
p . . .	0·0137	0·115	0·775	11·0	32·0	79·0	205·4	757·4

and for p in atm. and absolute temp., the results for the solid can be represented by $\log p = -13500/4{\cdot}57T + 7{\cdot}83$, and for the liquid, $\log p = -10100/4{\cdot}57T + 5{\cdot}49$. E. Ogawa gave:

	15·80°	26·95°	36·99°	40·01°	53·07°	70·15°	100·29°	130·00°
p . . .	5·37	11·03	21·05	25·09	47·12	100·18	300·46	746·18

The results for the solid can be represented by $\log p = -2542{\cdot}01T^{-1} + 9{\cdot}51791$. There is a **transition point** at 72°, and the results for the liquid below 72° can be represented by $\log p = -2167{\cdot}22T^{-1} + 8{\cdot}31658$; and above the transition temp. by $\log p = -1977{\cdot}39T^{-1} + 7{\cdot}77704$. The calculated **heats of vaporization** are:

	43·02° to 60·1°	60·10° to 85·22°	85·22 to 115·00°	115·00° to 130·00°
Heat vaporization .	9859	9763	9129	8982 cals.

H. von Wartenberg's value for the heat of vaporization is 10,100 cals. at the m.p. and 13,500 cals. for the **heat of sublimation** of the solid; E. Ogawa found 11,640 cals. for the heat of sublimation; 1540 cals. for the **heat of fusion**; P. Orzechowsky gave 3400 cals. per gram-mol., and H. von Wartenberg, 3·41 Cals. E. Ogawa gave 869 cals. for the **heat of transformation.** Again, **Trouton's constant** is 22·2, and the tetroxide is a normal liquid at its b.p. The **heat of formation** found by P. Orzechowsky, and H. von Wartenberg is 93·37 Cals. per atom of osmium. E. Ogawa calculated the **free energy** change from the solid to the liquid is 63 to 77 cals. at 25°. W. Herz studied some relations of the **entropy**. H. von Wartenberg gave 405° for the **critical temperature,** and E. Ogawa obtained a result between

388° and 422°—mean 405°. H. von Wartenberg gave 170 atm. for the **critical pressure** and 0·007 for the **critical volume.**

The **index of refraction** is 1·56 at 45°. J. Lifschitz and E. Rosenbohm studied the optical properties; A. Langseth and B. Qviller, the ultra-violet **absorption spectrum** of osmium tetroxide; and S. Kato measured the absorption spectrum of the vapour, and of its 0·001N-aq. soln. He found two groups of oscillation bands. In the first group, the intensity maxima appear at 2960 and 2947 A. in the gas, and at 2983 and 2970 A. in the soln. The maxima in the second group appear at 2475 and 2460 A. for the gas, and at 2515 and 2500 A. for the soln. The intensity of absorption in the first group is greater in the long-wave maxima, whilst in the second group the short-wave maxima are more intense. The shift of maxima towards the red in the spectra of the soln. is attributed to hydration. The effect of hydration is a linear function of the frequency for both sets of bands. H. Buff, and L. Bleekrode observed that soln. of the tetroxide do not conduct an **electric current**; M. le Blanc and H. Sachse said that the electrical conductivity is small; and H. von Wartenberg, that the sp. conductivity of the liquid is less than 10^{-11} mho.

H. von Wartenberg found that the characteristic odour of the tetroxide becomes perceptible when 2×10^{-5} mgrm. per c.c. is present. Osmium tetroxide is very easily reduced to osmium. H. St. C. Deville and H. Debray observed that the vapour of the tetroxide is easily reduced by **hydrogen**. K. A. Hofmann and co-workers noted that the tetroxide adsorbs hydrogen. J. J. Berzelius observed that osmium tetroxide may be sublimed in hydrogen, but if the hydrogen be mixed with the vapour and passed through a tube at a red-heat, the tetroxide is reduced in that region without explosion and does not extend to the colder parts of the mixture. F. C. Phillips said that no reduction occurs when hydrogen is passed into aq. soln. of the tetroxide. The tetroxide readily dissolves in **water**, and the aq. soln., said S. Tennant, and L. N. Vauquelin, does not redden litmus. H. von Wartenberg observed that water does not wet the oxide, yet 100 grms. of water dissolve 0·47 grm. of osmium tetroxide at 18°, and 100 grms. of carbon tetrachloride dissolve about 250 grms. of the tetroxide at 20°, so that the tetroxide can be extracted from aq. soln. by shaking the soln. with carbon tetrachloride, and recovered from the latter soln. by soda lye; osmium is precipitated from the soln. of alkali lye by treatment with platinized hydrogen. D. M. Yost and R. J. White found that the partition of osmium tetroxide between water and carbon tetrachloride is greatly diminished when the water contains sodium hydroxide, and slightly diminished when it contains potassium chlorate. It is inferred that **perosmic acid,** H_2OsO_5, is produced; and since $[H^{\cdot}][HOsO_5{}'] / [H_2OsO_5] = K = 8\times10^{-13}$ at 25°, the hypothetical perosmic acid is weaker than carbonic acid. E. Fritzmann studied the distillation of the tetroxide from its aq. soln. J. J. Berzelius observed that a mixture of hydrogen and steam reduces the oxide without explosion. A mixture of a soln. of osmium tetroxide and a strong **mineral acid** is yellowish-red, it smells of the tetroxide, and gives off the tetroxide when distilled. C. Claus observed that **hydrochloric acid** does not act on the tetroxide. J. Milbauer reported that osmium tetroxide is decomposed by conc. hydrochloric acid at room temp. with the evolution of chlorine, but O. Ruff and S. Mugdan said that the reaction does not take place with an acid of sp. gr. 1·124; and H. Remy showed that the reaction depends on the conc. of the acid. With hydrochloric acid of a sp. gr. greater than 1·160, osmium tetroxide is decomposed with an appreciable velocity, with the evolution of chlorine, forming quadrivalent, not bivalent, osmium. The result was confirmed by F. Krauss and D. Wilken, and R. Gilchrist. According to W. R. Crowell, and W. R. Crowell and H. D. Kirschman, when **hydrobromic acid** acts on octovalent osmium, at 100°, the products are quadrivalent osmium and bromine, and a state of equilibrium is attained; with conc. soln., 8N-HBr, the reaction to quadrivalent osmium and bromine is complete, and in dil. soln., 0·1N-HBr, the reaction is completed in the reverse direction. C. Claus, and

E. A. Klobbie found that iodine is quantitatively liberated from a soln. of **potassium iodide,** although N. A. Orloff observed that iodine is not liberated from a neutral soln. of the iodide, but, as shown by E. P. Alvarez, with acidic soln., iodine is liberated with the precipitation of $OsI_2.2HI$. K. A. Hofmann and co-workers found that osmium tetroxide influences the rate of decomposition of **potassium chlorate,** or of its aq. soln. The catalytic effect of the tetroxide in oxidation by alkali chlorate cannot be due to the formation of some higher osmium oxide, since osmium tetroxide does not take up oxygen from chlorate solutions, and the lower oxides of osmium take only as much oxygen from the chlorate as to give the tetroxide. Neither is it due to catalytic decomposition of the chlorate, since osmium tetroxide does not appreciably increase the velocity of evolution of oxygen from either solid chlorate or chlorate soln. The formation of an additive compound is evidenced by the following: (1) the solubility of potassium chlorate is increased in a solution of osmium tetroxide; (2) the addition of osmium tetroxide to a solution of potassium chlorate raises the oxidation potential to a point which is higher than that of either of the components; (3) the velocity with which iodine is liberated from a solution of potassium iodide indicates that the concentration of the active substance is proportional to the product of the concentrations of the osmium and chlorate. The chlorate is reduced directly to the chloride without the intermediate formation of chlorite or hypochlorite. This is due to the fact that the lower oxide of osmium formed during the process from the additive compound is Os_2O_5, or OsO_2,OsO_3, and this requires three oxygen atoms for the regeneration of osmium tetroxide. N. W. Fischer found that the tetroxide is not reduced in aq. soln. by **sulphur,** or by **selenium.** J. J. Berzelius, and H. Moraht and C. Wischin observed that **hydrogen sulphide** decomposes the dry oxide into osmium sulphide and water; and C. Claus, that the aq. soln. precipitates an oxysulphide, and that an aq. soln. acidified with hydrochloric acid forms osmium disulphide. J. J. Berzelius, and C. Claus and E. Jacoby observed that **sulphurous acid** added in increasing quantities progressively changes the colour yellow, brown, red, green, and finally indigo-blue—and sulphites are formed. J. J. Berzelius noted that a soln. of the tetroxide is slowly blackened by a large excess of aq. **ammonia,** and in a few hours when heated, at the same time nitrogen is evolved, and an ammino-oxide is formed. J. Fritzsche and H. Struve represented the reaction by the equation: $3OsO_4+10NH_3=6H_2O+2N_2+3\{OsO_2(NH_3)_2.H_2O\}$, and with a soln. of the tetroxide in alkali lye, osmiamic acid is formed. W. R. Crowell and H. D. Kirschman, and K. A. Hofmann and co-workers observed that **hydrogen sulphide** is quantitatively oxidized to sulphate by the tetroxide. W. R. Crowell and H. D. Kirschman reduced octovalent osmium to the quadrivalent state by **hydrazine,** in hydrobromic acid soln., and followed the reaction; $N_2H_4.H_2SO_4+H_2OsO_5+6HBr=N_2+H_2SO_4+H_2OsBr_6+5H_2O$, by electrometric titration. E. Frémy said that **potassium nitrite** transforms an alkaline soln. of the tetroxide into alkali osmate. S. Tennant, and N. W. Fischer found that **phosphorus** reduces a soln. of the tetroxide. K. A. Hofmann observed that **hypophosphorous acid** is oxidized to phosphoric acid by potassium chlorate in neutral or slightly acidic soln., in the presence of osmium tetroxide; and that whilst a mixture of **arsenic** and a soln. of potassium chlorate suffers no reaction even after the addition of a few drops of sulphuric acid, yet, on adding a trace of osmium tetroxide, the temp. rises, and the arsenic is oxidized to arsenic acid. It is thought that an additive compound of the tetroxide and the chlorate is formed, and that this is the real oxidizing agent. It is not thought probable that a higher oxide is formed as intermediate agent, and osmium tetroxide is not known to affect catalytically the decomposition of the chlorate. N. W. Fischer observed that **antimony** immersed in acidulated soln. of the tetroxide, acquires a solid film of osmium; and similarly with **bismuth.**

K. A. Hofmann and co-workers observed that colloidal **carbon** is oxidized vigorously by osmium tetroxide. L. J. Thénard observed that osmium tetroxide deflagrates on glowing coal like nitre. F. C. Phillips reported that the tetroxide is

rapidly reduced when heated in a current of **carbon monoxide ;** and also when heated with many **hydrocarbons**—heptane, ethylene, propylene, iso-butylene, acetylene, and allylene. O. Makowka found that osmium is not completely precipitated by passing acetylene into a dil. aq. soln. of osmium tetroxide ; but with a soln. of acetylene in acetone, a colloidal soln. of osmium is obtained from which the metal separates completely at 100° to 110°. F. Lehmann, and W. Normann and F. Schick showed that osmium tetroxide acts catalytically in the hardening or hydrogenation of **unsaturated oils** like linseed or cotton-seed oil. For the action of the tetroxide on fats, etc., *vide supra*, the uses of osmium. F. C. Phillips noted that the tetroxide is rapidly reduced by **carbonyl sulphide,** and by **methyl hydrosulphide,** or **sulphide.** J. J. Berzelius found that the tetroxide dissolves in **alcohol** or **ether,** forming a colourless soln. which deposits all the contained osmium in the course of a few hours, but an aq. soln. of the tetroxide is not decomposed by alcohol or ether. C. Claus said that in the case of alcohol, acetic acid, and dihydrated osmium dioxide are formed. According to J. J. Berzelius, if osmium tetroxide be placed on the edge of a piece of platinum foil, and held in the flame of a spirit lamp so as to allow the flame to rise freely in air, this part of the flame becomes luminous because the tetroxide formed by the combustion of the osmium is reduced by the flame to osmium and the finely-divided particles glow brightly in the flame. K. A. Hofmann and co-workers said that at 50° to 100°, and in oxygen at 10 atm. press., in the presence of a trace of osmium tetroxide, 40 per cent. alcohol is oxidized in 3 to 4 hrs. to acetic acid and aldehyde or acetal, traces of crotonaldehyde also being formed ; 50 per cent. methyl alcohol gives formaldehyde and formic acid. The action on the aldehydes takes place very slowly, or not at all ; for example, paracetaldehyde and acetal show no signs of oxidation within 8 days at 20° ; vanillin only after 24 hrs. E. Müller and J. Keil studied the catalytic dehydrogenation of formic acid. F. Döbereiner observed that **sodium formate** reduces a soln. of the tetroxide, neutralized with lime or potash, with the evolution of carbon dioxide and the formation of blue, colloidal metal ; and K. A. Hofmann and co-workers added that the acids, formic, acetic, and oxalic, are very stable towards osmium tetroxide. Aniline sulphate is readily oxidized, and anthracene gives anthraquinone in acetic acid soln. Osmium tetroxide is decomposed by **oil** or **tallow.** S. Tennant observed that organic substances are at first coloured purple and then black by osmium tetroxide—*vide supra*, the uses of osmium—and **tincture of galls** is coloured purple, and then dark blue owing to the formation of the " blue oxide." A. Butleroff found that **tannin** is blackened by the tetroxide. C. A. Mitchell recommended " osmic acid " as a reagent for the colorometric determination of pyrocatechol, pyrogallol, gallic acid, and corresponding tannins, and the subject was discussed by P. H. Price. F. Lehmann said that in hardening oils and fats, osmium tetroxide is converted into the dioxide, but W. Normann and F. Schick said that the metal is formed. According to C. Claus, a soln. of **cane sugar** is not reduced in 2 days in the cold, but at 30° to 60°, the hydrated dioxide is formed along with oxalic, formic, and carbonic acid ; **starch,** and **gum** behave like sugar, only the reaction proceeds more slowly ; and **indigo-blue** is oxidized. A. Butleroff observed that **salicin** is oxidized and the colour changes are : yellow→brown→black ; **uric acid** is quickly reduced at a gentle heat ; **turpentine** is reduced to a resin ; **mannite** is very slowly oxidized at ordinary temp. ; and **glycerol** is coloured blue. K. A. Hofmann and co-workers observed that in the presence of potassium chlorate in neutral or slightly acidic soln., and along with a trace of osmium tetroxide, **indigo-carmine** is oxidized to indigo-white, quinol to quinhydrone, aniline to emeraldin ; mono- and di-methylaniline are oxidized ; benzidine to diphenoquinone-di-imide, *p*-leucaniline and leucomalachite-green to the dyes ; catechol, resorcinol, and tannin are oxidized, anthracene to anthraquinone, ethyl alcohol to acetal, no chlorination taking place ; slightly acid potassium formate to carbon dioxide. K. A. Hofmann and co-workers observed that substances with the ethylene-linking, which readily add on ozone or halogens,

are attacked, but not so vigorously as in the case with permanganate. Thus, ethylene, propylene, amylene, indene, *r*-pinene, and dichloroethylene, CHCl : CHCl, are readily oxidized; trichloroethylene, $CHCl : CCl_2$, is only slowly oxidized, and perchloroethylene not at all. Allyl alcohol is much more readily oxidized than ethyl alcohol; *iso*eugenol is more readily oxidized than ethyl alcohol, whilst vanillin is not. Benzene containing thiophen gives a reaction due to the presence of the thiophen. Acetylene is oxidized. Benzoic acid, bromobenzoic acid, naphthalene, and saturated ketones are not affected, and benzaldehyde only very slowly. According to C. A. Mitchell, just as a substance must contain three hydroxyl-groups in juxtaposition to produce a permanent colour with iron salts—*i.e.* an ink—so also with osmium tetroxide, which yields an ink with gallotannic and gallic acids and with pyrogallol, but not with phenol or quinol. In very dilute solution osmic pyrogallate is at first violet, but almost immediately becomes greenish-blue, and when applied to paper gives a deep violet-black coloration. The reaction affords a sensitive test for osmium tetroxide, the distinctive blue coloration being obtained on adding a trace of solid pyrogallol to a solution containing a few drops of 1 per cent. osmium tetroxide solution. The vapour from boiling "osmic acid" solution will develop recent finger prints on paper, and conversely a slightly greasy finger print affords a test for osmium tetroxide, traces of organic substances left by the finger giving permanent grey to black colorations owing to the reduction of the osmium tetroxide to osmium. Amorphous **silicon** is not attacked by osmium tetroxide. W. R. Crowell and H. D. Kirschman titrated octovalent osmium salts in hydrobromic acid soln., electrometrically, with a **titanous salt** soln., and observed three inflexions in the curve—one corresponds with the reduction of the bromine to bromide ions, one with the reduction of octovalent to quadrivalent osmium, and one to the reduction of quadri- to tervalent osmium.

E. Frémy observed that when the vapour of osmium tetroxide is passed over red-hot **copper** turnings, metallic osmium is deposited on the copper; and if a current of hydrogen is passed along with the vapour of the tetroxide, the copper oxide is reduced, and the increase in weight of the copper is solely due to the osmium. The reaction is quantitative. S. Tennant observed that soln. of the tetroxide are reduced by nearly all the metals—**gold, rhodium, iridium,** and **platinum** are the exceptions, for they do not reduce the soln. The reduction occurs with **silver,** and with **mercury.** J. J. Berzelius observed that metals precipitate from the neutral aq. soln. only a small proportion of osmium together with the metal osmate, but in an acidulated soln., all the osmium is precipitated. According to N. W. Fischer, copper with an acidulated soln. gives a solid film of osmium without a blue tarnish; and silver immersed in the liquid becomes covered with various tints, and ultimately black, and this occurs in soln. so dil. that the odour is scarcely perceptible; silver thus tarnished does not lose its coating of osmium until it has been heated to redness. With acidulated soln., **zinc,** and **cadmium** precipitate osmium as a bluish- or reddish-black powder which remains suspended in the liquid for a long time and imparts to it a blue colour; if the zinc is in contact with platinum, the osmium is deposited as a reddish-grey film on the glass in the neighbourhood of the platinum. In acidulated soln. mercury does not give a blue coloration, and the osmium is deposited as a solid crust, which, according to S. Tennant, forms an amalgam. N. W. Fischer observed that **tin** colours an acidulated soln. of the tetroxide blue as it reduces the oxide to a suspension of finely-divided reduced osmium in the liquid; **lead** produces a solid crust of osmium and no blue soln.—the reduction is incomplete, and finally a white powder appears; and **iron** behaves like tin. J. J. Berzelius said that aq. soln. of osmium tetroxide do not expel carbon dioxide from **alkali carbonates.** N. W. Fischer observed that **ferrous sulphate** reduces an aq. soln. of osmium tetroxide, but not so with **stannous chloride.** H. Rose said that both salts reduce soln. of the tetroxide.

According to C. Claus, osmium tetroxide is not an acidic anhydride, and it does

not form salts with the alkalies. On the other hand, L. A. Tschugaeff said that the tetroxide performs the function of an acidic anhydride in forming salts with the alkali hydroxides. Thus, **potassium hydroxyperosmate,** $2KOH.OsO_4$, **rubidium hydroxyperosmate,** $RbOH.OsO_4$, and **cæsium hydroxyperosmate,** $CsOH.OsO_4$, and $CsOH.2OsO_4$, all furnish orange or brown crystals, which are readily soluble in water, and strongly hydrolyzed in aq. soln. F. Krauss and D. Wilken could not prepare these hydroxyperosmates by the method of L. A. Tschugaeff, but by adding sat. soln. of the hydroxides to solid osmium tetroxide, he obtained a potassium salt of the same composition as that given by L. A. Tschugaeff, but the cæsium salt had the composition $2CsOH.OsO_4$; and he obtained **ammonium hydroxyperosmate,** $2NH_4OH.OsO_3$, and **barium hydroxyperosmate,** $Ba(OH)_2.OsO_4$. These compounds form light brown or yellow crystals which decompose when separated from the mother-liquid. They contain octovalent osmium. F. Krauss and D. Wilken also prepared **cæsium difluoperosmate,** $2CsF.OsO_4$, and **rubidium difluoperosmate,** $2RbF.OsO_4$; but similar compounds were not formed with cyanides, thiocyanates, or organic bases. L. A. Tschugaeff obtained **rhodium dichloroquaterpyridino-hydroxyperosmate,** $[Rhpy_4Cl_2](OH)(OsO_4)_2$, in thin, yellow plates. The subject was discussed by E. K. Fritzmann.

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§ 7. The Osmium Fluorides

H. Moissan,[1] and O. Ruff and F. Eisner, observed that when fluorine attacks osmium (*q.v.*), fluorides are formed, and F. W. Tschirch isolated three fluorides from the products of the reaction. The composition of the mixed fluoride obtained by the action of fluorine on heated osmium, depends on the temp., the speed of the current of fluorine, and on the activity of the osmium, which, in turn, depends on the temp. to which the osmium oxide from which the osmium was obtained was heated. When the temp. is 250°, and the osmium is in an active form by having been prepared from an oxide which has not been heated to a high temp., the product contains hexa- and octo-fluorides only, and the relative proportion of the hexafluoride increases as the speed of the current of fluorine diminishes. At lower temp. with the less active forms of osmium, the product is mainly the tetrafluoride.

The isolation of **osmium octofluoride**, OsF_8, from the mixture of fluorides is effected by evacuating the containing platinum tube at ordinary temp., and collecting the condensate in a dry glass receiver cooled by liquid air. The ease of decomposition of the salt prevented H. Braune and S. Knoke studying the X-radiograms satisfactorily. According to O. Ruff and co-workers, the lemon-yellow crystals have a vap. density 11·4 (air unity) and the corresponding mol. wt. is 330 when the value for the octofluoride is 343. This result establishes the octovalency of osmium in this fluoride. The substance is solid at 34·1°, and a yellowish-red liquid at 34·7°, so the m.p. is near 34·4°. The vap. press., *p* mm., is:

	0°	20°	40·3°	47·5°	70°	100°
p . . .	159·6	302·7	594·5	760·0	1699·0	4944·0

The latent heat of vaporization between 38° and 54° is 20·6 cals. per gram, or 7101 cals. per mol. When the vapour is heated, it begins to decompose at 225°, but the decomposition becomes noticeable only above 400°. The vapour is colourless, and it has a peculiar odour; it vigorously attacks the mucous membrane of the nose, and eyes; it blackens organic substances where it touches; and the octofluoride produces a "burn" when it comes in contact with the skin. The solid fumes in air give a white cloud. The octofluoride forms a colourless soln. with water, and it is then more or less hydrolyzed because the liquid smells of the tetroxide and not the octofluoride. The hydrolysis was studied by N. V. Sidgwick. O. Ruff and co-workers observed no reaction with iodine. The vapour of the octofluoride blackens sulphur. Conc. sulphuric acid dissolves the vapour, forming a colourless soln. which smells of the tetroxide. Yellow phosphorus is blackened by the vapour,

but red phosphorus requires heating before a reaction occurs. Fluorides are formed with arsenic and with antimony. No reaction was observed with carbon, but organic substances are violently attacked by the octofluoride. It has a great tendency to attack the metals. The metals copper, silver, and gold lose their metal lustre, and acquire a black film. The gold is not attacked, but the other metals form fluorides. Magnesium reacts quickly; zinc, and mercury react slowly; aluminium reacts slowly; tin, and lead are quickly attacked: chromium reacts rapidly; manganese, iron and nickel react rapidly; and platinum behaves like gold. The soln. of the octofluoride in sodium hydroxide has the characteristic yellowish-red colour of the perosmates; and with alkali fluorides it forms white salts which are decomposed by sodium hydroxide with the evolution of ozonized oxygen.

When osmium, formed by reduction at a low temp., is treated with fluorine at 250°, the octofluoride being the most volatile passes along to a well-cooled receiver, and **osmium hexafluoride,** OsF_6, contaminated with other fluorides, collects close to where the tube leaves the furnace. This product is warmed in the platinum tube at 50°, and 20 mm. press., for about an hour, when the hexafluoride sublimes, and condenses on the cool part of the tube in light green crystals. The product is mixed with some osmium dioxide and tetroxide, and only an approximate determination of the physical properties has therefore been made. The m.p. is above 50° and below 120°, and it could not be determined accurately because the hexafluoride becomes black when heated in contact with glass; the b.p. is between 202° and 205°. The vapour in moist air is grey, and colours black all substances that are not quite dry—particularly the skin. The hexafluoride is decomposed by water, and by sulphuric acid, forming black osmium dioxide, the tetroxide and hydrofluoric acid. It forms yellow soln. with sodium hydroxide similar to that formed with sodium chlorosmate.

When osmium which has been reduced at a red-heat is treated with fluorine at 280°, a mixture of **osmium tetrafluoride,** OsF_4, and some higher fluorides is formed. These can be removed by passing nitrogen over the mixed fluorides at 100°, and at a low press. If the residue is extracted with water, the tetrafluoride dissolves. It was not isolated, but if hydrofluoric acid is added to the solution in the proportion of 2 mols. of acid to 1 mol. of fluoride, and the solution then neutralized with potassium hydroxide and evaporated, regular crystals are obtained, which are probably potassium osmifluoride. The fact that osmium is present in the aqueous extract in the quadrivalent condition was proved by titrating the sulphuric acid solution with permanganate, whereby oxidation takes place to the octovalent condition; the oxidized solution liberates iodine from potassium iodide, the osmium being reduced to the quadrivalent condition. The quantities of permanganate used and iodine liberated were equivalent. A similar method of analysis was also used with the hexafluoride. P. Henkel and W. Klemm gave 3·87 for the sp. gr. at −183°.

As indicated above, osmium octofluoride forms double salts with the alkali fluorides, but they have not been investigated; osmium tetrafluoride in soln. with hydrofluoric acid, and neutralized with sodium hydroxide, forms, on concentration, octahedral, tetrahedral, and dodecahedral, yellow crystals of **sodium fluosmate,** H_2OsF_6.

According to H. Moraht and C. Wischin, if osmium tetroxide be heated with an alcoholic soln. of hydrofluoric acid, a black powder of osmium oxyfluoride is formed.

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§ 8. The Osmium Chlorides

J. J. Berzelius [1] observed that when dry chlorine is passed over heated osmium, **osmium dichloride,** $OsCl_2$, is formed as a dark green sublimate, and farther away from the heated osmium, the more volatile, red tetrachloride sublimes. C. Claus and E. Jacoby found that the dark green colour is due to the presence of traces of moisture, for if the chlorine be thoroughly dried, the sublimate is dark blue. The needle-like crystals of the dark blue salt form an indigo-blue soln. with water, and on exposure to air it becomes green like the aq. soln. of the salt prepared by J. J. Berzelius, owing to the presence of the trichloride ; when exposed still more, the green soln. becomes yellow as it forms the tetrachloride. These transformations are retarded by the presence of alkalies which form double salts. C. Claus and E. Jacoby also said that hydrated osmium monoxide dissolves in hydrochloric acid, forming an indigo-blue soln. which rapidly oxidizes to the trichloride, and yellow tetrachloride.

These modes of preparing osmium dichloride were found by F. Bornemann, and O. Ruff and F. Bornemann, to furnish a mixture of chlorides ; and they prepared the dichloride by heating the trichloride to 500° under reduced press., and cooling the vapour to −50°. The product is a dark brown powder which is almost insoluble in water, but which yields a pale yellow soln. when boiled for a long time with water. W. Hampe observed that the dichloride sublimes without melting ; and that it dissolves slightly in ether, but more readily in water. The aq. soln. soon decomposes ; it is a good conductor of electricity, depositing osmous hydroxide at the cathode. The ethereal soln. is a non-conductor ; and the alcoholic soln. conducts slightly. According to O. Ruff and F. Bornemann, osmium dichloride is attacked slowly by conc. nitric acid, and aqua regia, forming osmium tetroxide ; and cold, conc. alkali lye slowly attacks it, forming a clear, deep brown soln. Osmium dichloride, unlike platinum dichloride, with conc. hydrochloric acid, does not form **chlorosmous acid,** H_2OsCl_4, analogous with chloroplatinous acid, H_2PtCl_4. W. Manchot and J. König prepared **osmium tricarbonyldichloride,** $Os(CO)_3Cl_2$. J. J. Berzelius did describe a **potassium chlorosmite,** obtained from soln. of the so-called osmium dichloride and potassium chloride, in light brown prisms. This product is now thought to have a more or less impure potassium chloroperosmite.

J. J. Berzelius prepared an aq. soln. of **osmium trichloride,** $OsCl_3$, by allowing a mixture of a sat. aq. soln. of osmium tetroxide, hydrochloric acid, and mercury to stand until the odour had disappeared ; and C. Claus and E. Jacoby, by the action of hydrogen sulphide on the hydrochloric acid soln. of the tetroxide. A salt can be isolated by adding ammonium chloride to this soln., but not osmium trichloride alone, since on evaporation over sulphuric acid, in vacuo, it yields a purple, shining mass, like varnish. H. Moraht and C. Wischin, however, obtained the *trihydrate,* $OsCl_3.3H_2O$, by heating osmium tetroxide with conc. hydrochloric acid in a reflux apparatus for 48 hours, a little alcohol being added to hinder the formation of perosmic anhydride ; chlorine was evolved, and a slight, black residue is left undissolved ; after filtering and evaporating in vacuo, large, well-formed, six-sided pyramids of the chloride $Os_2Cl_7.7H_2O$ were obtained. D. M. Bose and H. G. Bhar studied the magnetic properties.

According to H. Moraht and G. Wischin, this salt in moist air is dark olive-green, but when quite dry it is the colour of minium ; it dissolves in alcohol and water to give a dark green colour and crystallizes again unchanged. This chloride is a mixture of osmium tri- and tetra-chlorides, for, when its alcoholic soln. is mixed with a soln. of potassium chloride, red, octahedral crystals of potassium chlorosmate, K_2OsCl_6, separate, and if the filtrate from this be evaporated in vacuo, a crystalline residue of $OsCl_3.3H_2O$ is left. F. Bornemann, and O. Ruff and F. Bornemann prepared the anhydrous salt, admixed with some tetrachloride, by heating osmium at about 1050° in a current of chlorine, and cooling the vapour rapidly, and a product

of a higher degree of purity is obtained when ammonium chlorosmate is heated to 350° in chlorine. The brownish-black, microcrystalline powder, obtained as a sublimate, is hygroscopic, and freely soluble in water; the soln. is stable when boiled, although it possesses an acidic reaction; silver nitrate slowly precipitates a grey substance from the aq. soln. H. Dählmann studied the osmium halides; and I. I. Tscherniaeff, the complex salts. W. Manchot and J. König found that with dry or moist carbon monoxide, at 270°, osmium trichloride furnishes a crystalline sublimate, and when washed with boiling carbon tetrachloride, it furnishes **osmium tricarbonyldichloride,** $Os(CO)_3Cl_2$, which melts at 269° to 273°. L. A. Tschugaeff prepared red **osmium hexathiocarbamidotrichloride,** $[Os\{CS(NH_2)_2\}_6]Cl_3.H_2O$.

Osmium trichloride forms salts usually called *chlorosmites* or *osmochlorides*; here they are called **chloroperosmites,** $3RCl.OsCl_3$, or R_3OsCl_6. J. J. Berzelius described a brown double salt to be formed by allowing mercury to act on a sat. aq. soln. of osmium tetroxide and alkali lye mixed with hydrochloric acid, until the odour of the tetroxide had disappeared. The evaporation of the liquor furnishes the double salt mixed with some free potassium chloride. C. Claus and E. Jacoby said that **potassium chloroperosmite,** $K_3OsCl_6.3H_2O$, is formed when osmium mixed with potassium chloride is attacked by chlorine at an elevated temp. He obtained it by adding ammonia to an aq. soln. of osmium tetroxide in potash lye, adding hydrochloric acid before an osmiamate has separated, and rapidly evaporating the soln. to dryness. The salt mixed with ammonium and potassium chlorides is washed with ice-cold water. The dark red or reddish-brown crystals of the *trihydrate* effloresce in air and all the water is expelled at 150° to 180°. The salt is freely soluble in water to form a red soln. which has an astringent taste. The aq. soln. decomposes slowly when cold, rapidly when heated, with the separation of a brown oxychloride. W. Manchot and G. Lehmann found that the temp. of evolution of the halogen is depressed in the presence of carbon monoxide, but no carbonyl chloride is formed; but W. Manchot observed that if the chloride is heated in carbon monoxide, a carbonyl is sublimed. According to C. Claus, the salt is soluble in alcohol, and ether. Alkalies, and alkali carbonates give a precipitate of hydrated sesquioxide; aq. ammonia gives the same precipitate which redissolves, forming an ammine. Reducing agents turn the red soln. blue; and hydrogen sulphide precipitates a dark brown sesquisulphide. J. J. Berzelius obtained an impure **ammonium chloroperosmite,** $(NH_4)_3OsCl_6.3H_2O$, by the action of hydrochloric acid on an ammoniacal soln. of osmium tetroxide. The red liquor mixed with ammonium chloride is evaporated. The red or brownish-red crystals are soluble in water, and in alcohol. P. Mercier tried the salt as a developer for photographic plates.

J. J. Berzelius, and C. Claus and E. Jacoby obtained **osmium tetrachloride,** $OsCl_4$, as a reddish-brown sublimate, when osmium is heated in dry chlorine gas—*vide supra*, the dichloride. F. Bornemann, and O. Ruff and F. Bornemann recommended a temp. of 650° to 700°, and allowed the vapour to cool slowly in a tube wrapped in asbestos. The tetrachloride forms black, crystalline crusts, and it volatilizes in vacuo to a yellow vapour. S. M. Karim and R. Samuel studied the absorption spectrum. W. Hampe said that the tetrachloride fuses readily, and the fused mass is a non-conductor. W. D. Treadwell and M. Zürcher studied the electrometric titration of H_2OsCl_6. O. Ruff and F. Bornemann found that the tetrachloride is not hygroscopic, and it is decomposed by water very slowly to form hydrated osmium dioxide and hydrochloric acid. J. J. Berzelius said that the tetrachloride dissolves in a small quantity of water, forming a yellow soln. which turns green when mixed with a large proportion of water, then becomes opaque, depositing the dioxide. According to R. Gilchrist, the reaction between osmium tetroxide (*q.v.*) and 20 per cent. hydrochloric acid heated almost to boiling, in the presence of a little ethyl alcohol, furnishes in about 3 hrs. a soln. which does not smell of osmium tetroxide, and which changes from deep brown to transparent

reddish-yellow, and contains osmium tetrachloride. C. Claus and E. Jacoby observed that hydrochloric acid, or alkali chlorides, retard the hydrolysis. The tetrachloride is not soluble in the usual solvents, but dissolves in the strong oxidizing acids. L. Tschugaeff and E. Fritzmann boiled sodium chlorosmate with thiocarbamide in the presence of a little hydrochloric acid, and obtained an intense red coloration; they extracted **osmic hexathiocarbamidohydroxytrichloride,** $[Os(NH_2.CS.NH_2)_6]Cl_3(OH)$, and determined the f.p. and electrical conductivity of its aq. soln. O. W. Gibbs said that probably complex salts are formed when osmium chloride is treated with ammonium molybdate or sodium tungstate.

Osmium tetrachloride forms **osmichlorides** or **chlorosmates** of the type R_2OsCl_6, or $2RCl.OsCl_4$, with other metal chlorides. J. J. Berzelius, E. Jacoby, and C. Claus and E. Jacoby obtained **potassium chlorosmate,** K_2OsCl_6, by heating to near redness an intimate mixture of the finely-divided metal and potassium chloride in a current of chlorine. The chlorine is slowly absorbed, and to avoid a loss of osmium, the vapours are received in an alkaline soln. The black mass is washed with a little cold water to remove the excess of potassium chloride, and the product dissolved in hot water, and allowed to evaporate spontaneously for crystallization. The salt was obtained by C. Claus and E. Jacoby by boiling osmium tetroxide with hydrochloric acid, adding potassium chloride, and alcohol, and evaporating the liquid. K. Seubert, E. A. Sasserath, A. Rosenheim and E. A. Sasserath, K. Maisch, and A. Gutbier and K. Maisch obtained it by the double decomposition of the sodium salt with potassium chloride; and L. Wintrebert, by the action of hydrochloric acid on potassium osmyl oxynitrite. According to C. Claus, the dark red octahedral crystals are isomorphous with the corresponding salts of palladium, iridium, and platinum. R. Samuel and co-workers studied the absorption spectra of some complex chlorides. J. J. Berzelius observed that when the salt is ignited, it forms osmium and potassium chloride as a residue. It dissolves in cold water, forming a lemon-yellow soln., and more abundantly in hot water, forming a deep yellow soln. with a green tinge. The aq. soln. decomposes when it is boiled, forming osmium tetroxide and a black powder which C. Claus considered to be an **osmium oxychloride.** Paper moistened with the aq. soln. and exposed to sunlight acquires a blue colour which is not removed by washing. C. Claus observed that potassium iodide colours the liquid red. Hydrogen sulphide precipitates osmium sulphide. No chemical action occurs when the soln. is boiled with sulphurous acid, but C. Claus observed that the soln. in conc. sulphurous acid becomes dark green when heated, and a hydrated oxide is precipitated. C. Claus found that aq. ammonia precipitates the hydrated dioxide, and with a great excess of ammonia a soluble ammine is formed. H. Schwarz represented the reaction: $K_2[OsCl_6] \rightarrow [Os(NH_3)_2(OH)_2]$. O. W. Gibbs found that potassium nitrite does not reduce the soln. of the salt. According to J. J. Berzelius, when distilled with nitric acid, osmium tetroxide passes into the receiver, and potassium chloride and nitrate remain. C. Claus observed that sodium phosphate, and borax precipitate the hydrated dioxide. Alcohol precipitates the original salt from its aq. soln. as a vermilion red powder. H. Rose said that alkali formates reduce the liquid with the separation of osmium. According to C. Claus, potassium hydroxide precipitates the salt, and re-dissolves it when heated, forming a colourless soln. which becomes turbid and deposits the hydrated dioxide. H. Rose observed that silver nitrate, and mercurous nitrate form precipitates; C. Claus, that lead acetate has no action, and that ferrous sulphate reduces the soln. to metal. L. Brizard reduced potassium osmiamate with a hydrochloric acid soln. of stannous chloride at 60° and obtained a marron crystalline powder of **potassium amidochlorosmate,** $K_2Os(NH_2)Cl_5$. The crystals dissolve freely in water, forming a green soln. The aq. soln. readily decomposes into the tetroxide. The salt decolorizes potassium permanganate, and Fehling's soln.; and with silver nitrate, silver is deposited. A soln. in cold, conc. hydrochloric acid deposits crystals of **potassium amidohydrochlorosmate,** $K_2Os(NH_2)Cl_3.HCl$; the hot acid forms chlorosmate. L. Wintrebert obtained potassium nitrosylchloros-

mate, $K_2Os(NO)Cl_5$, by treating potassium nitritosmate with conc. hydrochloric acid. The red rhombic crystals are isomorphous with the corresponding salt of ruthenium. The salt is stable; it keeps very well in aq. soln. A. Rosenheim reported **potassium hydrosulphitochlorosmate,** $K_6H_2.OsCl_4(SO_3)_4$.

A. Gutbier and K. Maisch, and K. Maisch prepared **rubidium chlorosmate,** Rb_2OsCl_6, by adding rubidium chloride to the ammonium salt. The carmine-red, octahedral crystals are soluble in cold water, and the aq. soln. on exposure to air deposits a black powder. The salt is also soluble in hydrochloric acid. The corresponding **cæsium chlorosmate,** Cs_2OsCl_6, was obtained in a similar manner. F. Krauss and K. Mählmann prepared **palladium dichlorodiamminochlorosmate,** $[Pd(NH_3)_2Cl_2]OsCl_6$. J. J. Berzelius, F. Seybold, R. Gilchrist, K. Seubert, A. Rosenheim and E. A. Sasserath, and A. Gutbier and K. Maisch obtained **ammonium chlorosmate,** $(NH_4)_2OsCl_6$, by the double decomposition of the sodium salt with ammonium chloride; or by evaporating a soln. of osmium tetroxide in hydrochloric acid (*vide supra*) to a syrupy consistence, and adding ammonium chloride, when brick-red ammonium chlorosmate is precipitated. The brown, octahedral crystals are purified by recrystallization. According to R. Gilchrist, the sp. gr. is 2·93. The salt can be dried to constant weight at 140° to 150°; no evidence of decomposition can be detected below 170°. The salt is reduced to osmium sponge when heated in hydrogen. It is sparingly soluble in water; and is converted into spongy osmium when heated. L. Wintrebert said the reactions resemble those of the potassium salt.

L. Mehler, A. Gutbier and L. Mehler, K. Maisch, A. Gutbier and K. Maisch, and A. Gutbier and P. Walbinger, obtained **methylammonium chlorosmate,** $(CH_3NH_3)_2OsCl_6$, as brownish-red crystals; **dimethylammonium chlorosmate,** $\{(CH_3)_2NH_2\}_2OsCl_6$, as pale red, rhombic prisms; **trimethylammonium chlorosmate,** $\{(CH_3)_3NH\}_2OsCl_6$, as pale red, cubic crystals; **tetramethylammonium chlorosmate,** $\{(CH_3)_4N\}_2OsCl_6$, in reddish-yellow octahedra; **ethylammonium chlorosmate,** $(C_2H_5NH_3)_2OsCl_6$, as scarlet-red leaflets; **diethylammonium chlorosmate,** $\{(C_2H_5)_2NH_2\}_2OsCl_6$, as yellowish-red, monoclinic crystals; **triethylammonium chlorosmate,** $\{(C_2H_5)_3NH\}_2OsCl_6$, as orange-yellow or golden-yellow monoclinic crystals; **tetraethylammonium chlorosmate,** $\{(C_2H_5)_4N\}_2OsCl_6$, in red, monoclinic crystals; ***n*-propylammonium chlorosmate,** $(C_3H_7NH_3)_2OsCl_6$, in dark brown, monoclinic crystals; **iso-propylammonium chlorosmate,** $(C_3H_7NH_3)_2OsCl_6$, in brownish-red, monoclinic or rhombic prisms; **dipropylammonium chlorosmate,** $\{(C_3H_7)_2NH_2\}_2OsCl_6$, in reddish-yellow, monoclinic prisms; **tripropylammonium chlorosmate,** $\{(C_3H_7)_3NH\}_2OsCl_6$, in red, monoclinic crystals; ***n*-butylammonium chlorosmate,** $(C_4H_9NH_3)_2OsCl_6$, in brownish-red, monoclinic crystals; **iso-butylammonium chlorosmate,** $(C_4H_9NH_3)_2OsCl_6$, in yellowish-red monoclinic or rhombic crystals; **di-iso-butylammonium chlorosmate,** $\{(C_4H_9)_2NH_2\}_2OsCl_6$, in red crystals; **tri-iso-butylammonium chlorosmate,** $\{(C_4H_9)_3NH\}_2OsCl_6$, in red, triclinic crystals; **allylammonium chlorosmate,** $(C_3H_5NH_3)_2OsCl_6$, in reddish-brown, rhombic crystals; **di-iso-amylammonium chlorosmate,** $\{(C_5H_{11})_2NH_2\}_2OsCl_6$, in orange-yellow, rhombic crystals; **tri-iso-amylammonium chlorosmate,** $\{(C_5H_{11})_3NH\}_2OsCl_6$, in straw-yellow needles; **benzylammonium chlorosmate,** $(C_7H_7.NH_3)_2OsCl_6$, in brownish-red, monoclinic plates; **phenylammonium chlorosmate,** $(NH_3.C_6H_5)_2OsCl_6$, in brownish-red, rhombic leaflets; **phenylmethylammonium chlorosmate,** $(NH_2.CH_3.C_6H_5)_2OsCl_6$, in brownish-red, monoclinic crystals; **o-tolylammonium chlorosmate,** $(C_6H_4.CH_3.NH_3)_2OsCl_6$, in yellow or brownish-red, rhombic needles; **m-tolylammonium chlorosmate,** in brownish-red, rhombic needles; **p-tolylammonium chlorosmate,** in yellowish-red, rhombic leaflets; **o-4-xylylammonium chlorosmate,** $\{C_6H_3(CH_3)_2NH_3\}_2OsCl_6$, in red, monoclinic needles; **m-4-xylylammonium chlorosmate,** in ruby-red, rhombic crystals; **p-5-xylylammonium chlorosmate,** in red, rhombic needles; **α-naphthylammonium chlorosmate,** $(C_{10}H_7.NH_3)_2OsCl_6$, in brownish-red, rhombic plates; **β-naphthylammonium chlorosmate,** in brownish-red, rhombic leaflets; **ethylenediammonium chlorosmate,** $(C_2H_4N_2H_6)OsCl_6$, in dark brown, monoclinic crystals; **propylenediammonium chlorosmate,** $(C_3H_6N_2H_6)OsCl_6$, in brownish-red, monoclinic crystals; **pyridinium chlorosmate,** $(C_5H_6N)_2OsCl_6$, in red, rhombic plates; **guanidinium chlorosmate,** $\{C.NH(NH_2)_2H\}_2OsCl_6$, in dark brown crystals; **triphenylguanidinium chlorosmate,** $\{(C_6H_5)_3C.N(NH_2)_2H\}_2OsCl_6$, in yellow crystals; ***o*-amylanilinium chlorosmate,** $(C_6H_5.NH_2.C_5H_{11})_2OsCl_2$, in orange-yellow needles; ***m*-chloroanilinium chlorosmate,** $(C_6H_4ClNH_3)_2OsCl_2$, in reddish-brown, triclinic crystals; **tribenzylammonium chlorosmate,** $\{(C_6H_5.CH_2)_3NH\}_2OsCl_6$, in brownish-yellow, rhombic crystals; **ψ-cumidinium chlorosmate,** $\{C_6H_2(CH_3)_3NH_3\}_2OsCl_6$, in orange-red needles; **α-picolinium chlorosmate,** $(C_5H_4.CH_3.NH)_2OsCl_6$, in yellowish-red, rhombic leaflets; **β-picolinium chlorosmate,** in reddish-brown, monoclinic crystals; **lutidinium chlorosmate,** $\{C_5H_3(CH_3)_2NH\}_2OsCl_6$, in yellowish-brown, monoclinic crystals; **collidinium chlorosmate,** $\{C_5H_2(CH_3)_3NH\}_2OsCl_6$,

in brown, monoclinic crystals; **piperidinium chlorosmate**, $\{(CH_2)_5NH_2\}_2OsCl_6$, in pale brownish-red, rhombic crystals; **iso-quinolinium chlorosmate**, $(C_9H_7NH)_2OsCl_6$, in pale brownish-red, monoclinic crystals; and **quinolinium chlorosmate**, in yellowish-red, monoclinic needles.

C. Clauss and E. Jacoby, and K. Seubert prepared **sodium chlorosmate**, $Na_2OsCl_6.2H_2O$, by methods employed for the potassium salt. E. A. Sasserath, and A. Rosenheim and E. A. Sasserath prepared the salt as follows:

Sodium sulphitosmate was first prepared by passing sulphur dioxide through a soln. of osmium tetroxide in 20 per cent. soda lye, and when the soln. was nearly neutral to litmus, neutralizing the liquid with sodium hydrosulphite. This is converted into the chlorosmate by heating it in a current of hydrogen chloride, first at a gentle heat, and finally at dull redness, and also by boiling it with conc. hydrochloric acid of sp. gr. 1·19, and then evaporating the soln. to dryness on a water-bath, extracting with absolute alcohol, and distilling the alcoholic soln. under reduced press.

Sodium chlorosmate forms orange-red, rhombic prisms, easily soluble in water, and in alcohol. The salt forms a green soln. with a little water. According to G. Sailer, when boiled with a conc. soln. of sodium hyposulphite, it forms sodium sulphitosmate. When the soln. is treated with potassium chloride, it furnishes the corresponding potassium salt; similarly with ammonium chloride. The corresponding **alkaline earth chlorosmates** could not be obtained by double decomposition with the sodium salt. C. Claus and E. Jacoby obtained **silver chlorosmate**, Ag_2OsCl_6, by treating the potassium salt with silver nitrate. The dirty, greyish-green precipitate is insoluble in water, and soluble in aq. ammonia. The ammoniacal soln. was found by W. Eichler to deposit **silver diamminochlorosmate**, $Ag_2OsCl_6(NH_3)_2$, as a red powder which forms a yellow soln. with water. W. Eichler also obtained **zinc amminochlorosmate**, in orange-yellow rhombohedra, by the action of potassium chlorosmate on an ammoniacal soln. of zinc sulphate; similarly with **cadmium amminochlorosmate**, in yellow rhombohedra; **copper amminochlorosmate**, in yellow crystals insoluble in water and ammonia; **cobalt amminochlorosmate**, as a brown precipitate; and **nickel amminochlorosmate**, as a brown precipitate.

J. J. Berzelius, and C. Claus prepared **osmium oxydiamminochloride**, $[OsO(NH_3)_2]Cl_2$, by treating the hydroxide with hydrochloric acid. The brown, crystalline salt is soluble in water, and the aq. soln. decomposes and deposits a basic salt. When heated, the salt swells up, loses hydrogen chloride and ammonia, and leaves a residue of osmium.

The chlorine analogue of osmium hexafluoride, namely, **osmium hexachloride**, $OsCl_6$, has not been prepared, but E. A. Sasserath, and A. Rosenheim and E. A. Sasserath prepared the sodium derivative, **sodium osmium dodecachloride**, Na_6OsCl_{12}, or $6NaCl.OsCl_6$, by passing dry hydrogen chloride over warm sodium sulphitosmate—*vide supra*. The black product is dissolved in a small quantity of water, and recrystallized over sulphuric acid. The bright, copper-red leaflets are contaminated with a little sulphite. The addition of potassium chloride to the soln. does not yield **potassium osmium dodecachloride**, but rather K_2OsCl_6, nor could the potassium or **ammonium osmium dodecachloride** be formed by the direct method.

F. Krauss and D. Wilkins found that the brown soln. of osmium tetroxide in conc. hydrochloric acid, containing potassium iodide, contains **osmium hydroxytrichloride**, $Os(OH)Cl_3$. which crystallizes in brown needles containing water of hydration which is lost at 150°. This compound forms with alkali chlorides a series of hydroxypentachlorosmates, *e.g.* **potassium hydroxypentachlorosmate**, $K_2[Os(OH)Cl_5]$; **rubidium hydroxypentachlorosmate**, $Rb_2[Os(OH)Cl_5]$; **cæsium hydroxypentachlorosmate**, $Cs_2[Os(OH)Cl_5]$; **ammonia hydroxypentachlorosmate**, $(NH_4)_2[Os(OH)Cl_5]$; and **methylammonium hydroxypentachlorosmate**, $(CH_3NH_3)_2[Os(OH)Cl_5]$. When these salts are crystallized from conc. hydrochloric acid, the ordinary hexachlorosmates are formed.

O. W. Gibbs prepared **osmyl tetramminochloride,** $[OsO_2(NH_3)_4]Cl_2$, as an orange-yellow, crystalline precipitate, by adding ammonium chloride to a conc. soln. of potassium osmate. It yields spongy osmium when ignited. The salt is sparingly soluble in cold water, and it is decomposed in boiling water into osmium tetroxide and osmium oxydiamminochloride. It is insoluble in alcohol, in aq. soln. of ammonium salts, and in conc. hydrochloric acid; potassium ferrocyanide gives a violet coloration with an aq. soln. of the salt. P. Owsjannikoff recommended this salt in place of "osmic acid" for histological staining—*vide supra*, uses of osmium. Soluble, orange yellow crystals of **osmyl tetramminochloroplatinate,** $[OsO_2(NH_3)_4]PtCl_6$, were also prepared by O. W. Gibbs.

L. Wintrebert prepared **potassium osmyl chloride,** $K_2(OsO_2)Cl_4$, by the action of hydrochloric acid on potassium osmyl oxynitrite, and by the action of hydrochloric acid on potassium osmate; and by the action of boiling aqua regia on potassium chlorosmate. J. Hoard and J. D. Grenko found that the crystals of $K_2OsO_2Cl_4$ have a body-centred, tetragonal lattice with $a=6{\cdot}99$ A., and $c=8{\cdot}75$ A.; with two molecules per unit cell. The ions are $K^{\cdot}$ and OsO_2Cl_4''. The distances between the atoms Os and Cl is 2·28 A.; between Cl and Cl, 3·22 A.; between Os and O, 1·85 A.; and between O and Cl, 2·94 A. L. Wintrebert found that the red crystals are readily soluble in water, and when the conc. aq. soln. is cooled, red, octahedral, triclinic crystals of the *dihydrate* separate, and the water of crystallization can be expelled by heating the dihydrate in a current of hydrogen. When heated to 200° in hydrogen, osmium is formed. The neutral, aq. soln. is not stable, and forms osmic acid, but it is stable in the presence of an acid. Alkali lye, and hydrochloric acid transform the salt into a chlorosmate; and aq. ammonia forms **ammonium osmyl chloride,** $(NH_4)_2(OsO_2)Cl_4$, which can also be produced by methods analogous to those employed for the potassium salt. The garnet-red crystals of the ammonium salt are isomorphous with those of the potassium salt. L. Wintrebert prepared **ammonium osmyl oxydichloride,** $(NH_4)_2(OsO_2)OCl_2$, by adding hydrochloric acid to the corresponding nitrite; a slight excess of acid hinders oxidation by the nitrous fumes; and if the temp. is raised too high, ammonium osmyl chloride, or even chlorosmate, may be formed. If the mixture be gently warmed, nitrous fumes are evolved, and the salt is obtained as a yellow, crystalline deposit, slightly soluble in water. Potash lye converts the salt into ammonia, and potassium osmate. The corresponding **potassium osmyl oxydichloride,** $K_2(OsO_2)OCl_2$, could not be prepared because its oxynitrite is converted directly into the osmyl chloride by hydrochloric acid.

G. Scagliarini and Z. A. Masetti prepared what they regarded as **pyridinium trioxydichlorosmonate,** $(Hpy)_2[Os(H_2O)O_3Cl_2]$, by the action of pyridine hydrochloride on a strongly acidic soln. of potassium osmate. The yellowish-brown, fusiform needles yield potassium osmate when treated with conc. potash lye; they also prepared a salt, $[(OsO_3Cl_2)(H_2O)]H_2(C_5H_5N)_2$, by the action of pyridine hydrochloride on potassium osmate.

According to C. Claus, **osmium octochloride,** $OsCl_8$, is formed in small quantities when chlorine acts on osmium; and, according to H. Moraht and C. Wischin, when trihydrated osmium trichloride is heated in hydrogen, a yellow sublimate is formed thought to be octochloride. L. N. Vauquelin also suggested that the hydrochloric acid soln. of osmium tetroxide contains some octochloride. L. A. Tschugaeff obtained a complex **rhodium chloropyridinoperosmate,** $[Rh(C_6H_5N)_4Cl_2](OH).OsO_4$, in yellow plates.

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§ 9. The Osmium Bromides

H. Moraht and C. Wischin [1] observed that osmium, even when heated, is not attacked by bromine vapour; and when osmic acid is warmed with hydrobromic acid—and a little alcohol to prevent the formation of volatile tetroxide—a brown soln. is formed which, when evaporated in vacuo over sulphuric acid, and potassium hydroxide, furnishes crystals which when recrystallized appear in dark reddish-brown needles of the composition $Os_2Br_9.6H_2O$. The crystals are soluble in water, and in alcohol. They are a mixture of **osmium tribromide,** or **osmium tetrabromide** with some higher bromide. When the aq. soln. is evaporated on a water-bath, **osmium oxyfluoride** is formed.

E. A. Sasserath, and A. Rosenheim and E. A. Sasserath prepared **ammonium bromosmate,** $(HN_4)_2OsBr_6$, by the double decomposition of the sodium bromosmate and potassium chloride; L. Wintrebert, by the action of hydrobromic acid on potassium osmyl oxynitrite; and R. Gilchrist, by treating a soln. of osmium tetroxide (*q.v.*) in conc. hydrobromic acid, and evaporated to a syrupy consistence, with ammonium bromide. Dark brownish-black crystals of this salt were formed. The sp. gr. is 4·09. The salt can be dried at 140° to 150°; no evidence of decomposition can be detected below 170°. It is reduced by hydrogen to spongy osmium. A. Sachs observed that the black crystals belong to the cubic system. A number of organic bromosmates have been prepared by A. Gutbier and L. Mehler, A. Rosenheim and E. A. Sasserath, N. Pfanner, L. Mehler, and O. Edelhäuser.

The organic bromosmates include **methylammonium bromosmate,** $(CH_3.NH_3)_2OsBr_6$, in dark brown scales; **dimethylammonium bromosmate,** $\{(CH_3)_2NH_2\}_2OsBr_6$, in dark brown octahedra; **trimethylammonium bromosmate,** $\{(CH_3)_3NH\}_2OsBr_6$, in dark red octahedra; **tetramethylammonium bromosmate,** $\{(CH_3)_4N\}_2OsBr_6$, in dark reddish-brown octahedra; **benzalmethylammonium bromosmate,** $(CH_3.NH : CH.C_6H_5)_2OsBr_6$, as a dark red, crystalline powder; **benzylmethylammonium bromosmate,** $(CH_3.NH_2.CH_2.C_6H_5)_2OsBr_6$, in dark brown crystals; **ethylammonium bromosmate,** $(C_2H_5.NH_3)_2OsBr_6$, in dark reddish-brown, six-sided plates; **diethylammonium bromosmate,** $\{(C_2H_5)_2NH_2\}_2OsBr_6$, in dark brownish-red plates;

nitrosodiethylammonium bromosmate, $\{(C_2H_5)_2NO.NH\}_2OsBr_6$, in black, triclinic crystals; **triethylammonium bromosmate,** $\{(C_2H_5)_3NH\}_2OsBr_6$, in black crystals; **tetraethylammonium bromosmate,** $\{(C_2H_5)_4N\}_2OsBr_6$, in dark reddish-brown crystals; **benzalethylammonium bromosmate,** $(C_2H_5.NH:CH.C_6H_5)_2OsBr_6$, in black needles; **benzylethylammonium bromosmate,** $(C_2H_5.NH_2.CH_2.C_6H_5)_2OsBr_6$, in dark brown crystals; **n-propylammonium bromosmate,** $(C_3H_7.NH_3)_2OsBr_6$, in reddish-violet scales; **iso-propylammonium bromosmate,** in dark brown crystals; **dipropylammonium bromosmate,** $\{(C_3H_7)_2NH_2\}_2OsBr_6$, in copper-red plates; **tripropylammonium bromosmate,** $\{(C_3H_7)_3NH\}_2OsBr_6$, in dark brownish-red crystals; **n-butylammonium bromosmate,** $(C_4H_9.NH_3)_2OsBr_6$, in dark brown, six-sided plates; **iso-butylammonium bromosmate,** $(C_4H_9.NH_3)_2OsBr_6$, in reddish-violet, isotropic plates; **di-iso-butylammonium bromosmate,** $\{(C_4H_9)_2NH_2\}_2OsBr_6$, in dark brown, monoclinic crystals; **tri-iso-butylammonium bromosmate,** $\{(C_4H_9)_3NH\}_2OsBr_6$, in red needles; **allylammonium bromosmate,** $(C_3H_5.NH_3)_2OsBr_6$, in dark reddish-brown crystals; **iso-amylammonium bromosmate,** $(C_5H_{11}.NH_3)_2OsBr_6$, in dark reddish-brown crystals; **di-iso-amylammonium bromosmate,** $\{(C_5H_{11})_2NH_2\}_2OsBr_6$, in black, tetragonal prisms; **tri-iso-amylammonium bromosmate,** $\{(C_5H_{11})_3NH\}_2OsBr_6$, in dark reddish-brown crystals; **ethylenediammonium bromosmate,** $\{C_2H_4(NH_3)_2\}OsBr_6$, in black crystals; **propylenediammonium bromosmate,** $\{C_3H_6(NH_3)_2\}OsBr_6$, in black crystals; **guanidinium bromosmate,** $\{C.NH(NH_2)_2H\}_2OsBr_6$, in bronze plates; **triphenylguanidinium bromosmate,** $\{(C_6H_5)_3C.N(NH_2)H\}_2OsBr_6$, in dark red crystals; **anilinium bromosmate,** $(C_6H_5.NH_3)_2OsBr_6$, in black needles; **methylanilinium bromosmate,** $(C_6H_5.NH_2.CH_3)_2OsBr_6$, in dark brown, rhombic plates; **dimethylanilinium bromosmate,** $\{C_6H_5.NH(CH_3)_2\}_2OsBr_6$, in reddish-brown, six-sided plates; **ethylanilinium bromosmate,** $(C_6H_5.NH_2.C_2H_5)_2OsBr_6$, in black crystals; **diethylanilinium bromosmate,** $\{C_6H_5.NH(C_2H_5)_2\}_2OsBr_6$, in black crystals; **iso-amylanilinium bromosmate,** $(C_6H_5.NH_2.C_5H_{11})_2OsBr_6$, in black, pyramidal crystals; **benzalanilinium bromosmate,** $(C_6H_5.CH:NH.C_6H_5)_2OsBr_6$, in dark reddish-brown crystals; **benzylanilinium bromosmate,** $(C_6H_5.CH_2.NH_2.C_6H_5)_2OsBr_6$, in dark reddish-brown needles; **methylbenzylanilinium bromosmate,** $(C_6H_5.CH_2.NH_3.C_6H_5)_2OsBr_6$, in black crystals; **ethylbenzylanilinium bromosmate,** $(C_6H_5.CH_2.NH.C_2H_5.C_6H_5)_2OsBr_6$, in black monoclinic crystals; **o-bromoanilinium chlorosmate,** $(C_6H_4.Br.NH_3)_2OsCl_6$, in ruby-red needles; **m-bromoanilinium chlorosmate,** in reddish-brown needles; **p-bromoanilinium chlorosmate,** in dark red needles; **m-chloroanilinium bromosmate,** $(C_6H_4Cl.NH_3)_2OsBr_6$, as a dark brown powder; **p-chloroanilinium bromosmate,** in dark brown needles; **dichloroanilinium bromosmate,** $C(_6H_3Cl_2.NH_3)_2OsBr_6$, in black needles; **o-bromoanilinium bromosmate,** $(C_6H_4.Br.NH_3)_2OsBr_6$, in black needles; **m-bromoanilinium bromosmate,** in black crystals; **p-bromoanilinium bromosmate,** in black, monoclinic needles; **benzylammonium bromosmate,** $(C_6H_5.CH_2.NH_2)_2OsBr_6$, in black plates; **tribenzylammonium bromosmate,** $\{(C_6H_5.CH_2)_3NH\}_2OsBr_6$, in dark reddish-brown crystals; **o-toluidinium bromosmate,** $(C_6H_4.CH_3.NH_3)_2OsBr_6$, in reddish-brown needles; **m-toluidinium bromosmate,** in dark brown crystals; **p-toluidinium bromosmate,** in black needles; **dimethyl-o-toluidinium bromosmate,** $\{C_6H_4.CH_3.NH(CH_3)_2\}_2OsBr_6$, in black needles and plates; **dimethyl-p-toluidinium bromosmate,** in black crystals; **1, 2, 4-xylidinium bromosmate,** $\{C_6H_3(CH_3)_2NH_3\}_2OsBr_6$, in dark brown needles; **1, 3, 4-xylidinium bromosmate,** in dark brown needles; **1, 4, 5-xylidinium bromosmate,** in black needles; **ψ-cumidinium bromosmate,** $\{C_6H_2(CH_3)_3NH_3\}_2OsBr_6$, as a dark reddish-brown powder; **m-phenylenediammonium bromosmate,** $\{C_6H_4(NH_3)_2\}OsBr_6$, in black rhombic prisms; **1, 2, 4-toluylenediammonium bromosmate,** $\{C_6H_3.CH_3.(NH_3)_2\}OsBr_6$, in black needles; **1, 3, 4-toluylenediammonium bromosmate,** in black plates; **o-anisidinium bromosmate,** $(C_6H_4.O.CH_3.NH_3)_2OsBr_6$, in black plates; **p-anisidinium bromosmate,** in black, monoclinic needles; **o-phenetidinium bromosmate,** $(C_6H_4.O.C_2H_5.NH_3)_2OsBr_6$, in dark bronze needles; **p-phenitidinium bromosmate,** $(C_6H_4.O.C_2H_5.NH_3)_2OsBr_6$, in black plates; **pyridinium bromosmate,** $(C_5H_5.NH)_2OsBr_6$, in dark reddish-brown, rhombic plates; **α-picolinium bromosmate,** $(C_5H_5.CH_3.NH)_2OsBr_6$, in black, tetragonal plates; **β-picolinium bromosmate,** as a dark brown, crystalline powder; **lutidinium bromosmate,** $\{C_5H_3(CH_3)_2NH\}_2OsBr_6$, in black needles; **collidinium bromosmate,** $\{C_5H_3(CH_3)_3NH\}_2OsBr_6$, in black, triclinic crystals; **piperidinium bromosmate,** $(C_5H_{10}.NH_2)_2OsBr_6$, in dark brown needles; and **iso-quinolinium bromosmate,** $(C_9H_7.NH)_2OsBr_6$, as a dark brown, crystalline powder.

O. Edelhäuser, E. A. Sasserath, and A. Rosenheim and E. A. Sasserath prepared **potassium bromosmate,** K_2OsBr_6, by the double decomposition of the sodium salt with potassium chloride; and L. Wintrebert, by the action of hydrobromic acid on potassium osmyl oxynitrite. A. Sachs said that the brownish-black crystals belong to the cubic system. E. A. Sasserath said that the salt is sparingly soluble in water. L. Wintrebert prepared reddish-brown, rhombic crystals of **potassium nitrosylbromosmate,** $K_2Os(NO)Br_5$, by the action of hydrobromic acid on potassium nitritosmate. A. Rosenheim and E. A. Sasserath obtained **sodium bromosmate,** $Na_2OsBr_6.4H_2O$, by the action of dry hydrogen bromide, or of hydrobromic acid of sp. gr. 1·45, on sodium sulphitosmate. The

purple-red soln. deposits dark brown prisms of this salt. O. Edelhäuser prepared **rubidium bromosmate,** Rb_2OsBr_6, as a reddish-brown crystalline powder, by the action of rubidium chloride on the sodium salt soln.; and similarly also with **cæsium bromosmate,** Cs_2BrOs_6. R. Gilchrist prepared **silver bromosmate,** Ag_2OsBr_6, as a flocculent, indigo-blue precipitate, by adding silver nitrate to a soln. of the sodium salt. A pale brown precipitate of impure **strontium bromosmate,** and likewise of **barium bromosmate,** were obtained.

F. Krauss and D. Wilkins observed that when methylammonium hydroxypentachlorosmate is recrystallized from conc. hydrobromic acid, **methylammonium bromopentachlorosmate,** $(CH_3NH_3)_2[OsCl_5Br]$, is formed in deep red, six-sided leaflets; and with dil. hydrobromic acid, there is formed **methylammonium hydroxydibromotrichlorosmate,** $(CH_3NH_3)_2[Os(OH)Br_2Cl_3]$, which, with conc. hydrobromic acid forms **methylammonium trichlorotribromosmate,** $[CH_3NH_3)_2[OsCl_3Br_3]$. Only **methylammonium hydroxypentabromosmate,** $(CH_3NH_3)_2[Os(OH)Br_5]$, was obtained.

L. Wintrebert prepared **ammonium osmyl bromide,** $(NH_4)_2(OsO_2)Br_4$, in triclinic garnet-red crystals, by the action of hydrobromic acid on ammonium osmyl oxynitrite; and triclinic, garnet-red crystals of **potassium osmyl bromide,** $K_2(OsO_2)Br_4$, in an analogous manner. A yellow crystalline powder of **ammonium osmyl oxybromide,** $(NH_4)_2(OsO_2)OBr_2$, was prepared by the action of hydrobromic acid on ammonium osmyl oxynitrite.

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§ 10. Osmium Iodides

L. N. Vauquelin [1] did not succeed in getting iodine to unite with osmium when mixtures of the two elements were heated in a glass tube; and H. Moraht and C. Wischin added that there is no reaction between osmium and iodine vapour, or between osmic acid and iodine vapour. If osmium tetraiodide is reduced in hydrogen, a small yellow sublimate is formed which H. Moraht and C. Wischin assume to be **osmium diiodide,** OsI_2. According to E. P. Alvarez, and N. A. Orloff, potassium iodide, hydrochloric acid, and osmium tetroxide interact to form emerald-green **hydroiodosmous acid,** H_2OsI_4, or $OsI_2.2HI$. The compound is soluble in water, and more so in ether; it is insoluble in benzene, and in chloroform; the green soln. gradually becomes red on exposure to air; and the red colour appears when the green soln. is treated with oxidizing acids—*e.g.* nitric acid; and acidic soln. with nitrites deposit black hydrated dioxide; a soln. of permanganate, and acidic soln. of a chromate, are decolorized by the green soln. The reaction can be utilized in detecting osmium—*vide supra.* When the soln. is treated with an excess of potassium iodide, **potassium iodosmite,** K_2OsI_4, is formed.

H. Moraht and C. Wischin reported **osmium tetraiodide,** OsI_4, to be formed by heating osmic acid on a water-bath with conc. hydriodic acid. The osmic acid slowly dissolves, forming a brown soln. which is stable in the cold; and when evaporated in vacuo over potassium hydroxide, and sulphuric acid, and subsequently recrystallized, it furnishes violet-black, rhombohedral crystals. The crystals are hygroscopic; and they are readily soluble in water, and alcohol.

When the reddish-brown soln. in alcohol is warmed, it deposits black pulverulent **osmium oxyiodide.**

L. Wintrebert prepared **potassium iodosmate,** K_2OsI_6, by the action of conc. hydriodic acid on potassium osmyl oxynitrite; the reaction is vigorous, nitrous fumes and iodine vapour are evolved. When the brownish-violet soln. is allowed to stand, it deposits dark violet octahedra. The salt is rather more soluble in water than the corresponding chloro- and bromo-osmates, and it quickly decomposes. The presence of a little free hydriodic acid hinders the decomposition of the aq. soln. It is stable in hydrogen up to 200°, but near 300°, hydrogen iodide is evolved. When potassium nitritosmite is treated with hydriodic acid, it forms **potassium nitrosyliodosmate,** $K_2Os(NO)I_5$, in dark brown crystals isomorphous with the corresponding chloro- and bromo-salts. L. Wintrebert also prepared **ammonium iodosmate,** $(NH_4)_2OsI_6$, in a manner analogous to that employed for potassium iodosmate. The salt furnishes bluish-black octahedra, which are less soluble than those of the potassium salt.

L. Wintrebert did not succeed in preparing complex **osmyliodides.**

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§ 11. The Osmium Sulphides and Sulphates

J. J. Berzelius [1] observed that when a mixture of osmium and sulphur is heated in a retort, the metal burns brightly in the sulphur vapour, to form **osmium sulphide.** Hydrogen sulphide was found by J. J. Berzelius, and C. Claus and E. Jacoby to precipitate osmium sulphides from hydrochloric acid soln. of osmium salts. The products are all dark brown, and form dark yellow (colloidal) soln. with water; they dissolve in nitric acid, forming a sulphate when the osmium sulphide is in excess, but with warm nitric acid, osmium tetroxide is given off, and a sulphate is formed. H. St. C. Deville and H. Debray boiled an ammoniacal soln. of osmium tetroxide saturated with hydrogen sulphide, and found that the osmium sulphide which is formed inflames at a high temp., and volatilizes as sulphur dioxide and osmium tetroxide. V. N. Ivanoff observed no complex formation with thiocarbamide.

J. J. Berzelius prepared **osmium disulphide,** OsS_2, by the action of hydrogen sulphide on a soln. of potassium chlorosmate; E. Frémy, by the action of the gas on a soln. of potassium osmate; and H. Moraht and C. Wischin, by passing a current of hydrogen sulphide over warm, dry osmium oxysulphide—at a higher temp. the reaction is very vigorous. H. G. Krall, and L. Wöhler and co-workers also prepared this sulphide. According to I. Oftedal, the X-radiogram of osmium disulphide corresponds with a cubic lattice of the pyrite type, with $a=5\cdot64$ A., and a calculated density of 9·44. K. Meisel gave $a=5\cdot6075$ A., and a calculated density of 9·57. According to R. Juza, the dissociation press. of sulphur vapour at 944° is 27 mm., and at 1044°, 215 mm.; the thermal value of the reaction $OsS_2=Os+S_2(gas)$ at 1020° is -62 Cals. The subject was discussed by V. M. Goldschmidt, P. Niggli, and L. Pauling and M. L. Huggins. R. Juza gave 9·47 to 9·48 for the observed sp. gr.

J. J. Berzelius, and C. Claus obtained **osmium tetrasulphide,** OsS_4, as a brown precipitate, by the passage of hydrogen sulphide through an acidified soln. of the tetroxide. The dark brown precipitate is insoluble in water and in soln. of alkali sulphides, hydroxides, or carbonates. It rapidly oxidizes on exposure to air, and at high temp. it leaves a residue of osmium. When ignited in vacuo, it becomes

incandescent, decrepitates, and forms **osmium hemipentasulphide,** Os_2S_5, or $OsS_2.OsS_3$, as a grey substance with a metallic lustre. R. Juza tried to prepare a higher sulphide by the action of hydrogen sulphide on soln. of osmium tetroxide in different proportions of hydrochloric acid, and found the composition of the precipitates to be with 26·7 per cent. of hydrochloric acid, $OsS_{3\cdot58}O_{0\cdot18}.0{\cdot}14H_2O$; with 17·3 per cent. of acid, $OsS_{3\cdot65}O_{0\cdot13}.0{\cdot}27H_2O$; and with 1·1 per cent. of acid $OsO_{3\cdot06}O_{0\cdot8}.0{\cdot}47H_2O$. When the precipitated sulphide is heated, there is an abrupt development of heat as osmium disulphide crystallizes. E. Fritzmann and E. M. Zuhn found that neither hydrogen dioxide nor ammonium persulphate oxidizes osmium tetrasulphide in neutral or acidic soln., but with a mixture of both reagents, a slight oxidation occurs ; in acidic soln., chlorates and bromates have a powerful oxidizing action, whilst perchlorates are rather less active.

C. Claus said that when an aq. soln. of osmium tetroxide is treated with hydrogen sulphide, a dark brown precipitate of **osmium oxysulphide** is formed. C. Claus gave the formula $OsOS_3.nH_2O$; E. von Meyer gave $Os_3O_5S_7.2H_2O$. H. Moraht found that hydrogen sulphide acts vigorously, and with incandescence, on dry osmic acid with the formation of **osmium oxydihydrosulphide,** $Os_2O_3(SH)_2$, in accord with the reaction : $2H_2OsO_4+4H_2S=Os_2O_3(SH)_2+5H_2O+2S$. Osmium oxydihydrosulphide is a brown powder ; and it is decomposed and dissolved by hydrochloric, sulphuric, and nitric acids. The temp. of the reaction shows that the hydrogen is not likely to be present as water of hydration. The acidic nature of the hydrogen is shown by the evolution of carbon dioxide when the oxysulphide dissolves in a soln. of sodium carbonate ; by the evolution of hydrogen sulphide when the oxysulphide is treated with an acid ; with solid potassium sulphide, it forms a yellow substance with the escape of hydrogen sulphide ; and when heated with ethyl iodide it forms mercaptan in accord with the equation :

$$\begin{array}{c} O{=}Os{-}SH \\ \dot{O} \\ O{=}\dot{O}s{-}SH \end{array} + 2C_2H_5I = 2HI + \begin{array}{c} O{=}Os{-}SC_2H_5 \\ \dot{O} \\ O{=}\dot{O}s{-}SC_2H_5 \end{array}$$

C. Claus obtained **osmous sulphite,** $OsSO_3$, in black, insoluble crystals, by the action of sulphur dioxide on a soln. of osmium tetroxide—**10**. 57, 25—and A. Rosenheim and E. A. Sasserath, and E. A. Sasserath found that with a soln. of osmium tetroxide in dil. soda lye, **sodium sulphitosmate,** $3Na_2O.OsO_3.4SO_2.5H_2O$, is formed ; and with potash lye, **potassium sulphitosmate,** $11K_2O.4OsO_3.14SO_2.7H_2O$, is produced. Sodium hydrosulphite acts on sodium chlorosmate at its b.p., forming white crystals of **sodium hexasulphitosmate,** $Na_8[Os(SO_3)_6].8H_2O$; with an excess of sulphite and allowing the soln. to stand in the cold for several weeks, yellow or brown, acicular crystals of **sodium dichlorotetrasulphitosmate,** $Na_6(OsCl_2(SO_4)_4].10H_2O$, are formed ; and if the mixed soln. is gently warmed **sodium chloropentasulphitosmate,** $Na_7[OsCl(SO_4)_5].6H_2O$, is formed. They also reported **potassium hydrochlorosulphitosmate,** $[OsCl_4(SO_3)_4]K_6H_2$.

Definite information about the osmium sulphates is not available. J. J. Berzelius reported **osmous sulphate** to be formed by the action of nitric acid on an excess of osmium sulphide ; and by similarly treating osmium disulphide, he obtained **osmium disulphate.** Some observations were also made by C. Claus and E. Jacoby.

C. Claus and E. Jacoby, and J. J. Berzelius reported **osmium oxydiamminosulphate,** $[OsO(NH_3)_2]SO_4$, to be formed by the action of dil. sulphuric acid on the corresponding hydroxide ; and O. W. Gibbs, **osmyl tetramminosulphate,** $[(OsO_2)(NH_3)_4]SO_4$, by the action of ammonium sulphate on potassium osmate. The yellow crystals are sparingly soluble in cold water, and are decomposed by boiling water.

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§ 12. Some Nitrogen Compounds of Osmium

No **osmium nitrate** has been reported, but **osmium oxydiamminonitrate,** $[OsO(NH_3)_2](NO_3)_2$, was prepared by C. Claus and E. Jacoby,[1] and J. J. Berzelius by the action of dil. nitric acid on the corresponding hydroxide ; and O. W. Gibbs obtained **osmyl tetramminonitrate,** $[(OsO_2)(NH_3)_4](NO_3)_2$, in yellow crystals which are very unstable.

J. Fritzsche and H. Struve prepared what has been called **osmiamic acid,** $NHOsO_3$, by treating the barium salt with dil. sulphuric acid, or the silver salt with hydrochloric acid. The yellow soln. can be concentrated to a certain extent, but it decomposes at a certain stage in the process of concentration. The soln. of osmiamic acid is strongly acidic, it decomposes alkali carbonates with the evolution of carbon dioxide ; and when heated, it gives off osmium tetroxide. J. Fritzsche and H. Struve regarded it as a compound of perosmic acid with osmium nitride to which they gave the name *osman*, and hence they called it *osman-osmic acid*, and represented its composition $H_2N_2Os_2O_5$; C. Gerhardt showed that this formula is incorrect ; and A. Joly represented it by the formula $HNOsO_3$, and he suggested that it is a nitroso-compound, $OsO(NO)OH$, derived from an unknown trihydroxy-compound, $Os(NO)(OH)_3$, analogous to the ruthenium compound, $Ru(NO)(OH)_3$. This hypothesis is in harmony with some of the reactions of the acid, and with L. Brizard's observation that acidulated stannous chloride reduces it to the amide, $K_2Os(NH_2)Cl_5$—L. Brizard gave the formula NO.OsO.OK. A. Werner and K. Dinklage, however, showed that well-cooled hydrochloric acid reacts with the potassium salt to form $KOsNOCl_5$, a fact confirmed by L. Wintrebert. A. Werner and K. Dinklage suggested that it is unlikely that a nitroso-group is present in the original acid, and they favour the hypothesis that the acid has an imido-group replacing an atom of oxygen in osmium tetroxide ; and that the potassium salt is a tautomeric form :

$$\begin{matrix} O \\ O \end{matrix}\!\!>\!Os\!<\!\!\begin{matrix} O \\ NH \end{matrix} \qquad\qquad \begin{matrix} O \\ KO \end{matrix}\!\!>\!Os\!\lesseqgtr\!\!\begin{matrix} O \\ N \end{matrix}$$

Osmiamic acid, $HNOsO_3$ Potassium osmiamate, $KNOsO_3$

J. Fritzsche and H. Struve prepared **ammonium osmiamate,** $(NH_4)NOsO_3$, by decomposing the silver salt with ammonium chloride. The crystals are freely soluble in water, and alcohol ; and decompose explosively at 150° F. M. Jäger and J. E. Zanstra found that the rhombic crystals have a lattice with 4 mols. per unit cell, and with a=5·53 A., b=5·86 A., and c=13·54 A. H. Dufet said that the crystals are tetragonal octahedra, and isomorphous with those of **potassium osmiamate,** $KNOsO_3$, prepared by J. Fritzsche and H. Struve, by the action of

ammonia on a cold soln. of osmium tetroxide in potash lye. A. Joly kept the temp. at 40°. H. Dufet found that the orange-yellow, tetragonal octahedra are ismorphous with those of the ammonium salt. F. M. Jäger and J. E. Zanstra observed that the tetragonal, bipyramidal crystals of potassium osmiamate have the axial ratio $a : c = 1 : 2{\cdot}3123$; the vol. of the elementary cell is 417·6 cubic A.; the observed sp. gr. is 4·49 to 4·51; and the value calculated from the cell, with 4 mols. of $KOsNO_3$, is 4·616. According to J. Fritzsche and H. Struve, the salt is soluble in water, and in alcohol, but insoluble in ether. The salt is partially decomposed on recrystallization from aq. soln. When heated in vacuo, A. Joly observed that nitrogen is evolved at 200°, potassium osmate, and osmium dioxide are formed at 350°, and at 440°, the residue has the composition $KOsO_3$, a kind of *potassium hyposmate*. F. M. Jäger and J. E. Zanstra found that the rhombic crystals of **rubidium osmiamate,** $RbNOsO_3$, have 4 mols. per unit cell, and that $a=5{\cdot}57$ A., $b=5{\cdot}84$ A., and $c=13{\cdot}64$ A.; and similarly for **cæsium osmiamate,** $CsNOsO_3$, for which $a=8{\cdot}08$ A., $b=8{\cdot}35$ A., and $c=7{\cdot}22$ A.; for **thallous osmiamate,** $TlNOsO_3$, for which $a=5{\cdot}42$ A., $b=5{\cdot}68$ A., and $c=13{\cdot}54$ A. J. Fritzsche and H. Struve prepared **sodium osmiamate,** $NaNOsO_3.nH_2O$, by the action of ammonia on a soln. of osmium tetroxide in soda lye; or by the double decomposition of the silver salt and sodium chloride. The yellow crystals are very soluble in water, and in alcohol. A soln. of osmium tetroxide in an ammoniacal soln. of a salt of silver furnishes **silver osmiamate,** $AgNOsO_3$, in lemon-yellow crystals. The salt is soluble in water, and in aq. ammonia. It detonates violently at 80°, or by percussion. The action of barium chloride on a soln. of the silver salt furnishes **barium osmiamate,** $Ba(NOsO_3)_2$, in yellow, shining needles which are soluble in water, and detonate at 150°. A soln. of **zinc osmiamate,** $Zn(NOsO_3)_2$, was prepared, but not the solid. and when a zinc salt is added to a soln. of osmium tetroxide in ammonia, or a soln. of the potassium salt in ammonia, a light yellow, crystalline powder, **zinc tetramminosmiamate,** $Zn(NOsO_3)_2.4NH_3$, is formed. It is decomposed by cold or hot water, and is insoluble in aq. ammonia. It can be dried in air without decomposition. J. Fritzsche and H. Struve also prepared **mercurous osmiamate,** $HgNOsO_3$, as an amorphous, light yellow precipitate which is insoluble in water and does not explode when heated; **mercuric osmiamate,** $Hg(NOsO_3)_2$, in prismatic crystals which quickly decompose; and **lead osmiamate,** $Pb(NOsO_3)_2$, by treating a soln. of an osmiamate with lead acetate; the dirty yellow precipitate soon becomes purple, and gives off osmium tetroxide. If a soln. of an osmiamate is treated with lead nitrate no precipitation occurs, but after some time, crystals are formed which rapidly decompose.

The osmium nitrites were inadvertently omitted from **8**. 49, 38. L. Wintrebert[2] prepared **osmium nitrite,** $Os(NO_2)_2$, by decomposing barium nitritoperosmite, with the theoretical proportion of dil. sulphuric acid, and by working in the cold, the evolution of nitrous fumes can be avoided The liquid is supposed to contain **nitritoperosmous acid,** $H_2Os(NO_2)_5$, and when concentrated, it evolves nitrous fumes and deposits osmium nitrite as a brown powder, stable in air. O. W. Gibbs, and L. Wintrebert observed that **potassium nitritoperosmite,** $K_2Os(NO_2)_5$, is produced by the action of an excess of potassium nitrite on a soln. of the chlorosmate, at 80°; in air, osmyl nitrite is formed. The canary-yellow parallelopipeds are readily soluble in water. By double decomposition of sodium nitrite with the barium or silver salt, orange-yellow crystals of **sodium nitritoperosmite,** $Na_2Os(NO_2)_5.2H_2O$, soluble in water, were obtained; **ammonium nitritoperosmite,** $(NH_4)_2Os(NO_2)_5.2H_2O$, was obtained in orange-yellow crystals; **silver nitritoperosmite,** $Ag_2Os(NO_2)_5.2H_2O$, in golden-yellow crystals; **calcium nitritoperosmite,** $CaOs(NO_2)_5.4H_2O$, in orange-yellow crystals; **strontium nitritoperosmite,** $SrOs(NO_2)_5.2H_2O$, in orange crystals; and **barium nitritoperosmite,** $BaOs(NO_2)_5.H_2O$, was obtained in yellow plates by the action of barium chloride on a non-aqueous soln. of potassium nitritoperosmite above 15°—below 15°, the salt is tetrahydrated. Similarly, **magnesium nitritoperosmite,** $MgOs(NO_2)_5.4H_2O$,

in sulphur-yellow crystals; and **zinc nitritoperosmite,** $ZnOs(NO_2)_5.\frac{1}{2}H_2O$, in orange-yellow crystals, were prepared.

According to L. Wintrebert, when osmium tetroxide is reduced by nitric oxide in the presence of potassium nitrite, there is formed **potassium osmyl nitrite,** $K_2(OsO_2)(NO_2)_4$; and by cooling a warm soln. of potassium osmyl chloride and potassium nitrite. The crystals decompose in sunlight, in aq. soln., and in contact with potash lye. Ammonia forms **osmyl tetramminonitrite,** $[(OsO_2)(NH_3)_4](NO_2)_2$. If a conc. soln. of potassium nitrite acts on osmium tetroxide, **potassium osmyl oxynitrite,** $K_2(OsO_2)O(NO_2)_2.3H_2O$, is formed; and also when nitric oxide acts on a soln. of a mol. of osmium tetroxide and 2 mols. of potassium hydroxide; and by the action of potassium hydroxide on the osmyl derivative. The salt forms brownish-black needles which dissolve in potash lye to form potassium osmate; they are slightly soluble in cold water; they begin to lose water of crystallization at 35°; when crushed in a mortar, the odours of osmium tetroxide and of nitrogen peroxide can be detected; and at 200°, in hydrogen, osmium is formed without explosion. L. Wintrebert also prepared **ammonium osmyl oxynitrite,** $(NH_4)_2(OsO_2)O(NO_2)_2$, with 1, 3, and 4 mols. of water respectively; **sodium osmyl oxynitrite,** $Na_2(OsO_2)O(NO_2)_2$, as a syrupy liquid; **silver osmyl oxynitrite,** $Ag_2(OsO_2)O(NO_2)_2.H_2O$; **barium osmyl oxynitrite,** $Ba(OsO_2)O(NO_2)_2.4H_2O$; and **strontium osmyl oxynitrite,** $Sr(OsO_2)O(NO_2)_2.3H_2O$.

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CHAPTER LXXIII

IRIDIUM

§ 1. The Occurrence of Iridium

THE history of iridium has been indicated in connection with the platinum metals. Iridium occurs in nature alloyed in small quantities with the platinum metals. Iridium occurs as osmiridium or iridiosmium—*vide* platinum; and as an alloy of platinum and iridium. In the gold mines of the Urals, R. Hermann [1] found a black magnetic substance which he called *irite* and which was considered by J. J. Berzelius, and G. A. Kenngott to be an iridium osmite, but was proved by C. Claus to be a mixture of chromite, iridiosmium, and ferric oxide associated with the oxides of osmium, iron, and chromium. J. Prinsep found that a sample from the auriferous sands of the Ava, in Burma, had 60 per cent. of iridium, 20 per cent. of platinum, and the remainder mainly iron. M. F. Heddle called it *avaite*. The subject was discussed by H. Burney. L. F. Svanberg reported 1·09 to 2·52 per cent. of iridium—not as osmiridium—in platinum ore from Choco, equatorial Colombia, H. St. C. Deville and H. Debray, 0·85 to 1·55 per cent.; and T. Thomson, 72·9 per cent. in ore from Brazil; H. St. C. Deville and H. Debray, 0·85 to 4·20 per cent. in the ore from California, A. Kromayer, 0·70 per cent., F. Weil, 3·10 per cent., S. Kern, 0·01 to 0·60 per cent., and I. Koifman, 1·38 to 6·72 per cent. of iridium in ore from various mines in the Urals; H. St. C. Deville and H. Debray, 0·40 per cent. in the ore from Oregon; P. Collier, 0·62 per cent. in the ore from Plattsburg, New York; G. C. Hofmann, 1·04 to 1·21 per cent. in the ore from British Columbia, Canada; M. Böcking, 0·66 per cent. in the ore from Borneo, and S. Bleekrode, 6·13 per cent.; J. J. Berzelius, 2·35 to 4·97 per cent. in Russian ores, G. Osann, 1·91 per cent., H. St. C. Deville and H. Debray, 1·45 to 4·30 per cent.; C. Claus, 0·98 per cent., and S. Kern, 0·11 to 2·80 per cent., L. Duparc and M. Tikonowitch, and N. Wissotsky, 0·55 to 2·68 per cent. in the ore from Tagil; 0·27 to 1·55 per cent. in the ore from the watershed of the river Iss-Swetli-Bor and Weressowy-Ouwal, 1·22 to 7·54 per cent. in ore from Kamenouchky, Koswinsky, Kanjakowsky, Omountnaïa, and Daneskin-Kamen, 0·24 to 1·65 per cent. in ore from Goussewi-Kamen, Kiedrowka, Barantchia, and Solwa; and 0·24 to 1·19 per cent. in ore from Goussewka, Schoumuka, and Obleiskaya-Kamenka; H. St. C. Deville and H. Debray, 0·95 per cent. in ore from Spain, and 1·10 to 2·2 per cent. in ore from Australia; J. C. H. Mingaye, 27·79 per cent. in ore from New South Wales. The occurrence of osmiridium, and iridiosmium in these ores has been discussed in connection with osmium, and platinum. A. Cissarz noted the occurrence of iridium in the copper shales of Mansfeld.

The general occurrence of iridium has been discussed in connection with the platinum metals. F. W. Clarke and H. Washington's [2] estimate of the proportion of iridium in the igneous rocks of the earth's crust is of the order $n \times 10^{-10}$ per cent., and I. and W. Noddack gave $3{\cdot}0 \times 10^{-12}$ for the earth's crust; $2{\cdot}3 \times 10^{-5}$ for meteoric iron; $5{\cdot}0 \times 10^{-6}$ for troilite; and for the atomic distribution, oxygen unity, $3{\cdot}2 \times 10^{-7}$; and later, they gave $2{\cdot}1 \times 10^{-8}$ for the earth's crust, and $0{\cdot}9 \times 10^{-6}$ for meteorites. The subject was discussed by P. Niggli, P. Vinassa, V. M. Goldschmidt and C. Peters, and F. Bernauer. J. M. Davison, G. P. Merrill, and J. C. H. Mingaye observed iridium in meteoric iron. H. A. Rowland, and

J. N. Lockyer discussed the presence of iridium in the sun's photosphere. M. N. Saha, H. von Klüber, and C. E. St. John classed iridium amongst the elements of doubtful occurrence in the fixed stars.

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§ 2. The Extraction and Preparation of Iridium

The recovery of osmiridium was studied by G. H. Stanley and H. R. Adam.[1] The opening up of platinum ores with aqua regia is discussed in connection with platinum ; and the opening up of the osmiridium ore and the volatilization of osmium as the tetroxide was discussed in connection with ruthenium and with osmium. According to L. N. Vauquelin, and J. J. Berzelius, the black powder remaining after treatment of the ore with aqua regia was mixed in a retort with twice its weight of potassium nitrate. Osmic acid distils over. The operation is repeated, if necessary, on any black powder which remains after treatment with hydrochloric acid ; this soln. is mixed with nitric acid, and distilled for osmium tetroxide—*vide* osmium. The liquor in the retort is diluted with water, nearly neutralized with ammonia, and the filtered liquid is evaporated and treated with ammonium chloride, for iridium chloroiridate. The mixed precipitate of ammonium chloroiridate and chloroplatinate, when ignited furnishes a powder containing platinum, which is soluble in dilute aqua regia, and iridium, which is virtually insoluble in that liquid.

The separation of iridium was also described by F. Wöhler, J. Persoz, C. Claus, M. C. Lea, O. W. Gibbs, H. St. C. Deville and H. Debray, C. A. Martius, S. P. Sadtler, A. Bettendorff, W. von Schneider, and R. Bunsen. In the treatment of osmiridium, after removing the osmium as tetroxide by distillation, the residue contains iridium

contaminated with more or less ruthenium (*q.v.*). The soln. is evaporated to a small bulk, and treated with ammonium chloride and nitric acid, and evaporated to dryness on a water-bath. The residue is washed with a soln. of ammonium chloride, about half saturated, until the washings are colourless, and the resulting ammonium chloroiridate dried and heated to redness in hydrogen. The residue is digested with aqua regia to remove platinum, and osmium if present; and then fused with potassium nitrate and hydroxide and leached with water to remove potassium ruthenate. The insoluble residue is then heated white-hot to volatilize the last traces of osmium.

When finely-divided iridium or iridium sponge is fused with lead an alloy is produced from which platinum, palladium, and some rhodium are removed by digestion with aqua regia. The ruthenium and iron at the same time form an alloy with iridium. This alloy is crystalline and is difficult to dissolve. The process was employed by H. St. C. Deville and J. S. Stas, and H. St. C. Deville and H. Debray, and they also used zinc in place of lead for opening up osmiridium. G. Matthey purified the iridium still containing a small proportion of platinum, rhodium, ruthenium, and iron as follows:

The powder is fused with ten times its weight of lead for some hours. The cold mass is treated with nitric acid to remove the lead, and the residue is digested with aqua regia to remove platinum. There remains iridium associated with rhodium, ruthenium, and iron, which is then fused at a high temp. with potassium hydrosulphate and the cold product washed with water to remove the rhodium. The remaining iridium is then fused for a long time with 10 times its weight of potassium hydroxide and 3 times its weight of potassium nitrate in a gold crucible. The iron is oxidized, the iridium forms insoluble potassium iridate and the ruthenium, soluble potassium ruthenate. The product is washed with an alkaline soln. of sodium hypochlorite until the washings are no longer coloured, and then allowed to remain suspended in a cold soln. of sodium hypochlorite for some time. The mixture is boiled in a retort until the distillate no longer reddens a dil. alcoholic soln. of hydrochloric acid. The residue is again heated with potassium nitrate and an alkaline soln. of sodium hypochlorite saturated with chlorine to remove the last traces of ruthenium. To remove iron and traces of ruthenium, and rhodium, the residue is dissolved in aqua regia, evaporated to dryness, extracted with water, and the filtered soln. is slowly poured into a conc. soln. of sodium hydroxide and hypochlorite. The liquid should remain clear; and it is distilled in a current of chlorine, and received in a dil. alcoholic soln. of hydrochloric acid. When the distillate shows no coloration, ruthenium is absent. The chlorine precipitates most of the iridium as blue oxide which is washed, dried, and reduced by ignition in a porcelain tube in a current of carbon dioxide and monoxide obtained by the action of sulphuric on oxalic acid. When the product is fused at a red-heat with potassium hydrosulphate, iron and rhodium are removed when the product is washed with water; washing with chlorine water removes gold; and washing with hydrofluoric acid removes silica derived from the alkalies, or from the containing vessels. The iridium can be fused in charcoal, and cast into an ingot. G. Matthey said that even with the utmost care. the resulting iridium retains minute traces of oxygen, rhodium, ruthenium, and possibly iron. N. W. Perry discussed the fusion, casting, and dephosphorization of iridium; and J. Holland, and W. L. Dudley, the fusion of iridium.

U. Antony recommended the following process:

Iridium is precipitated by zinc to an acidified soln. of iridium trichloride, and digested with conc. nitric acid, of sp. gr. 1·35, containing some nitrous acid, to eliminate osmium and palladium, and then digested with dil. aqua regia ($1HNO_3$, $3HCl$, and $3H_2O$) to dissolve platinum and any traces of osmium and palladium. The washed residue is fused with potassium hydrogen sulphate to remove rhodium. The insoluble iridic oxide left is reduced by hydrogen in the cold, the metal converted into potassium chloriridate, and purified by repeated crystallization. The metal obtained in this way still contains platinum, but on passing a current of chlorine and carbon monoxide over it at a temp. of 250°, a small quantity of yellow crystals sublimes, which when treated with water evolve carbonic anhydride and hydrogen chloride and leave a black powder consisting of platinum. The iridium is left as a dark-green powder containing iridium and chlorine, and is entirely free from platinum.

E. Leidié recommended the following process for the purification of iridium:

Iridium purified by fusion with lead is finely-powdered, mixed with twice its weight of fused sodium chloride, and heated to incipient redness in a current of dry chlorine. The cooled product is treated with very dil. hydrochloric acid, and the filtered soln. is heated

to 50° to 60°, and mixed with successive small quantities of sodium nitrite until the evolution of nitrogen oxides ceases and the liquid becomes neutral to litmus. It is then carefully mixed with sufficient sodium carbonate to make it alkaline to litmus, and with a slight excess of sodium nitrite, boiled for a few minutes, cooled and filtered; iron, lead, and gold are precipitated, whilst the soln. contains sodium osmate, Na_2OsO_4; and the complex nitrites of iridium, $Ir(NO_2)_3.3NaNO_2$; ruthenium, $Ru(NO_2)_3.3NaNO_2$; and rhodium, $Rh(NO_2)_3.3NaNO_2$. A slight excess of sodium hydroxide is then added, and the soln., after cooling, is sat. with chlorine, heated gently, and treated with a rapid current of chlorine to eliminate ruthenium and osmium in the form of peroxides. The residual liquid is repeatedly evaporated with hydrochloric acid to decompose nitrites, nitrates, and chlorates, and the residue dissolved in cold chlorine water and crystallized to remove sodium chloride. The final crystalline separations are a mixture of sodium chlororuthenate and sodium chloroiridate; these are carefully dried, heated in dry chlorine at 440°, cooled, and treated with cold chlorine water. Ruthenium chloride remains undissolved, whilst the iridium passes into soln., and can be precipitated in the form of ammonium chloroiridate. The successful separation of iridium and ruthenium depends on obtaining the double chlorides free from any excess of sodium chloride, and on drying very carefully both the chlorine and the mixture of double chlorides.

E. Wichers and co-workers, and R. Gilchrist and co-workers recommended the following process:

The dried material is added to a mixture of sodium hydroxide and dioxide which has been fused to expel moisture, and the mixture kept fused for 2 to 3 hrs. with occasional stirring if practicable. The molten mass is poured on an iron plate from which it separates cleanly on cooling. Leaching the melt with cold water dissolves some iridium in the form of a sodium salt but leaves most of it as an insoluble oxide or possibly a sodium salt. Nearly all of the osmium and most of the ruthenium present will be in the alkaline soln., but much ruthenium remains with the iridium, as do also the other platinum metals in whole or in part, and base metals such as iron and nickel. Much of the ruthenium remaining with the iridium may be removed by treating the residue with sodium hypochlorite soln.—*vide supra*, G. Matthey's process. The residue is digested with hydrochloric acid on the steam-bath for several hours and the resulting soln. of iridium chloride decanted. A fresh portion of hydrochloric acid is added to insure extracting all of the soluble iridium compounds. The unattacked residue from this treatment is again fused with alkali, or, if rhodium is predominant, it is mixed with sodium chloride and heated in a current of chlorine—*vide* rhodium.

The repeated precipitation of ammonium chloroiridate is a suitable method for freeing iridium from most of the impurities it may contain, the notable exceptions being platinum and ruthenium. The chief disadvantage of this scheme is the trouble involved in redissolving the iridium salt. This can be done by suspending it in hot water and saturating with sulphur dioxide. The iridium salt is rather easily dissolved because of its reduction to soluble compounds of tervalent iridium. This method of dissolution has the further advantage of precipitating much of the rhodium, if more than small amounts are present, as a slightly soluble double sulphite. The resulting soln., filtered from any precipitate, is evaporated with an excess of hydrochloric acid to decompose the sulphite compounds. The residue is taken up with water and treated with chlorine or aqua regia, ammonium chloroiridate being precipitated. Some ammonium chloride is added to the soln. to replace any of this salt that has been destroyed and to decrease the solubility of the double salt. Ammonium chloroiridate can also be decomposed by prolonged heating with aqua regia or chlorine. This treatment may be more tedious than the use of sulphur dioxide, but it results in the complete destruction of the ammonium radical and also tends to remove small amounts of osmium as the volatile tetroxide. Platinum cannot be eliminated by the repeated precipitation of ammonium chloroiridate. Ruthenium persists with the iridium also, in spite of the greater solubility of its ammonium salt. Most of the ruthenium present with iridium can be removed by pouring the soln. of the chlorides into an excess of sodium hydroxide, saturating the resulting mixture with chlorine and distilling off ruthenium tetroxide—*vide* ruthenium. Repeating the distillation several times will produce iridium very nearly free from ruthenium, but the strictly complete removal of the latter element is very difficult, if not impossible, by this method.

E. Wichers and co-workers obtained good separations of ruthenium and iridium by a process—described by J. Fritzsche and H. Struve, C. Claus, M. C. Lea, and O. W. Gibbs—based on the relatively greater ease with which ruthenium is precipitated by hydrogen sulphide:

A soln. containing about 37 grms. of iridium as chloride, 25 ml. of hydrochloric acid, in 700 ml., was saturated with hydrogen sulphide at room temp. It was set aside for about 60 hrs., after which the soln. was filtered off and treated further with hydrogen sulphide

for several hours, the temp. being kept not far from the b.p. The soln. was set aside overnight and then filtered from the precipitated sulphides. The metals precipitated by the two treatments amounted to somewhat less than 15 per cent. of the total metal in the soln. Upon pouring the residual iridium soln., first reoxidized with chlorine, into an excess of sodium hydroxide soln. and distilling with chlorine, no ruthenium was found in the distillate.

It is extremely difficult to separate the almost inappreciable traces of ruthenium and rhodium from iridium. The spectroscopic detection of impurities in iridium is not so convenient as is the case with some other platinum metals because the spectrum of iridium is complex and many of the sensitive lines of the other platinum metals are coincident with iridium lines unless great dispersion is used. I. Wada and T. Nakazona, and E. Wichers and co-workers observed that soln. of titanous salts will completely precipitate rhodium and platinum in the presence of iridium. S. T. Aoyama found that platinum, accompanied by 1 to 3 per cent. of the total iridium, is completely precipitated from acidic soln. of the chlorides by metallic copper. The precipitate can be heated in hydrogen, and treated with aqua regia which dissolves the platinum but not the iridium. B. G. Karpoff found that if a mixture of ammonium chloroplatinate and chloroiridate is reduced at 100°, by mercury, the platinum, accompanied by 0·04 to 0·11 per cent. of iridium, is precipitated; he also recommended a process of separating rhodium and iridium by fusion with bismuth; and V. V. Lebedinsky, by boiling a soln. with potassium iodide. B. G. Karpoff and A. N. Fedorova studied the separation of platinum and iridium; and K. Hessner, the recovery of iridium.

H. Debray prepared **crystalline iridium** by heating the metal with pyrite and borax, and extracting the product with dil. hydrochloric acid. It is assumed that iridium sulphide is formed and decomposed in the operation. H. Rössler obtained crystals by cooling silver-iridium alloys. When ammonium chloroiridate is ignited, **iridium sponge** is formed. According to E. Wichers and co-workers, if the ignition is done in air the sponge is partly oxidized. This is easily corrected by igniting and cooling the sponge in hydrogen. S. G. S. Dicker prepared **iridium films** by the thermal decomposition of the carbonyl; and G. F. Taylor, **iridium filaments** by drawing the molten metal in glass tubes.

When an alkaline soln. of iridium hemitrioxide is boiled with alcohol, **iridium black** is deposited, as indicated by J. W. Döbereiner, and R. Böttger. J. J. Berzelius used formic acid as the reducing agent. Iridium black is an indefinite mixture of finely-divided iridium and its oxides. When iridium black is ignited it forms iridium sponge. G. R. Levi and R. Haardt discussed the structure of the powder; and A. A. Pollitt, and I. I. Tschukoff and co-workers, its catalytic properties. The so-called **explosive iridium,** discovered by R. Bunsen,[2] is produced when an alloy of iridium and zinc is treated with hydrochloric acid to remove the zinc. The iridium remains in a finely-divided condition—*vide* platinum. E. Cohen and T. Strengers attribute the explosiveness to the union of hydrogen and oxygen occluded in the metal, since the metal is not explosive in the entire absence of air; and the metal ceases to be explosive if it is kept for several days at 100° to 200°.

G. Hofmeier,[3] and A. Gutbier and G. Hofmeier obtained **colloidal iridium** or **iridium hydrosol** by reducing an aq. soln. of the chloride with hydrazine hydrate in the presence of gum arabic as protective colloid. C. Paal and C. Amberger used sodium amalgam as reducing agent, and sodium protalbate or lysalbate as protective colloid. C. Paal used hydrogen, sodium formate, and formaldehyde as reducing agents for the colloid. When the soln is evaporated over conc. sulphuric acid in vacuo, the solid hydrosol is obtained; it dissolves in warm water reproducing the colloidal soln. When the colloidal soln. is shaken with barium sulphate or animal charcoal, the dispersed metal is coagulated and precipitated. G. A. Brossa obtained a colloidal soln. by sparking iridium electrodes immersed in ice-cold water with a current of 20 to 25 amps. and 220 volts. The colour of the hydrosol ranges

from red to black. A small current favours the formation of the black soln. J. Donau observed that a borax bead is coloured reddish-brown by colloidal iridium.

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§ 3. The Physical Properties of Iridium

The **colour** of compact iridium has a brilliant greyish-white surface, between that of silver and tin ; and native iridium is silver-white with a tinge of yellow, and it is grey on a fractured surface. Native iridium which, according to A. Breithaupt,[1] is always contaminated with platinum, occurs in cubic **crystals.** P. W. Jeremejeff observed that cubic crystals are rare ; the iridium generally occurs in angular grains. Twinning occurs about the (111)-plane, commonly in polysynthetic groups. The cubic cleavage is indistinct. Osmiridium, or iridosmium—which contains besides osmium, and iridium, ruthenium, rhodium, and platinum—forms, according to G. Rose, hexagonal plates. G. D. Preston studied the twinning of the crystals. H. Debray, and H. Rössler prepared artificial crystals which are

octahedral. The hexagonal forms of some iridium alloys is taken by G. Rose, and A. Lévy to show that iridium is dimorphous, but W. Prinz observed that all the specimens of the hexagonal variety which he examined are distorted octahedra belonging to the cubic system. A. W. Hull found that the **X-radiograms** correspond with a face-centred, cubic lattice, and that the side of the unit cell has a=3·805 A., with 2·690 A. as the shortest distance between the atoms. R. W. G. Wyckoff gave a=3·823 A.; and T. Barth and G. Lunde, a=3·823 A., and there are 4 atoms per unit cell. E. A. Owen and J. Iball, and E. A. Owen and E. L. Yates gave a=3·8314 A., and calculated that the closest approach of the atoms is 2·709 A. T. Barth and G. Lunde, G. Natta, and V. I. Iveronova studied the subject. L. Holborn and co-workers observed that compact iridium which had been heated to 1670° exhibited on the surface a net-work of lines which was taken to indicate a change of structure, and after heating to 2130°, much coarser-grained crystals were formed. Scattered over the surface were a number of crater-like protuberances, produced by the evolution of gas from the metal. J. A. Harker also observed these little eruptions or volcanoes coming through the surface 20° below the f.p. They are produced by occluded gases, and little bits of metal may be shot off. L. Tonks observed the anchoring of the cathode spot on a discharge tube by iridium projecting through a mercury surface.

J. G. Children gave 18·680 for the **specific gravity** of a porous globule of iridium; and R. Bunsen, 15·19. R. Hare gave 21·78 to 21·83 for the sp. gr. of compact iridium; H. St. C. Deville and H. Debray, 21·15 and 22·421 at 17·5°; G. Matthey, 22·38; and L. Holborn and co-workers, 22·41. P. W. Jeremejeff found for the native cubic crystals 22·647 to 22·668, and for octahedral crystals 22·770 to 22·773 from Sukho-Wisim, near Nischne-Tagilsk, and 22·8053 to 22·8361 for crystals from New Yansk; and G. Rose gave 22·65. J. J. Berzelius gave 15·8629 for the sp. gr. of iridium sponge reduced in hydrogen; and G. Rose, 18·6088 for the sp. gr. of iridium black. A. W. Hull calculated from the X-radiograms a sp. gr. of 23·15 when the best representative value of the observed results is 22·42. R. Bunsen said that iridium is harder than iron. V. M. Goldschmidt calculated 1·352 A. for the **atomic radius.** E. H. Westling, J. C. Slater, G. Hägg, W. Biltz and K. Meisel, J. A. M. von Liempt, P. Vinassa, and L. Pauling studied the atomic constants.

I. R. Rydberg gave 6·5 for the **hardness** of the metal on Mohs' scale; and on Brinell's scale, 172; and C. A. Edwards gave 217. According to J. J. Berzelius, and R. Bunsen, iridium is very brittle, so that when struck with a hammer it shatters into small pieces having a fine-grained fracture; and it can be powdered by trituration. It is difficult to work mechanically, to polish, and to draw into wire. E. Grüneisen found for the **elastic modulus** of iridium, E=52,500 to 52,900 kgrms. per sq. mm. at 17·5° to 19°; and E. Widder gave $E=E_{20}\{1-0·0004274(\theta-20)\}$. C. Schäfer observed that the **torsion modulus** of iridium decreases 4·03 per cent. per 100° rise of temp. E. Grüneisen calculated the **compressibility** coeff. of iridium to be $0·28\times10^{-12}$ c.g.s. units. P. W. Bridgman gave for the compressibility $(0·268-1·3\times10^{-6}p)\times10^{-6}$ at 30°, and $(0·281-2·2\times10^{-6}p)\times10^{-6}$ at 70°. L. H. Adams gave $0·27\times10^{-6}$ megabars. G. A. Tomlinson, and R. von D. Wegener studied the internal cohesion.

H. Fizeau [2] observed the coeff. of **thermal expansion** to be $0·0_570$ at 40°, and $0·0_5708$ at 50°, increasing by $0·0_879$ per degree. R. Benoit found the coeff. a, at $\theta°$ between 2° and 80° to be $a=0·0_56358+0·0_83210\theta$; L. Holborn and S. Valentiner, $l=l_0(1+0·0_5669670\theta\pm0·0_81158\theta^2)$; and E. Grüneisen, $0·0_5568$ between −190° and 17°, and $0·0_5658$ between 17° and 100°. S. Valentiner and J. Wallot found:

	−192° to −158°	−158° to −124°	−73° to −55°	−55° to −33°	−33° to −20°	−13° to 0·6°	−0·6 to 19°
a .	$0·0_5443$	$0·0_5522$	$0·0_5585$	$0·0_5619$	$0·0_5640$	$0·0_5638$	$0·0_5672$

T. Barratt and R. M. Winter gave for the coeff. of **thermal conductivity** 0·141 cal. per cm. per sec. per degree at 17°, and 0·135 at 100°.

H. V. Regnault [3] found the **specific heat** of iridium to be 0·04186 between 20° and 100°. J. Violle gave for the mean sp. ht. between 0° and θ°, $c=0{\cdot}0317+0{\cdot}0_5 6\theta$, or 0·0323 between 0° and 100°, and 0·0401 between 0° and 1400°. U. Behn found 0·0303 between −79° and 18°, and 0·0282 between −186° and 18°; and J. Dewar, 0·0099 between −253° and −196°. F. M. Jäger and E. Rosenbohm measured the true sp. ht. of iridium, c_p, and these values with those for the sp. ht. at constant vol., c_v, as well as the corresponding atomic heats, C_p and C_v, are:

	0°	100°	300°	600°	900°	1200°	1500°	1700°
c_p . .	0·0307	0·0315	0·0329	0·0352	0·0374	0·0396	0·418	0·0433
c_v . .	0·0303	0·0310	0·0322	0·0342	0·0362	0·0381	0·401	0·0413
C_p . .	5·928	6·083	6·353	6·797	7·222	7·647	8·072	8·361
C_v . .	5·851	5·980	6·218	6·604	6·990	7·357	7·840	7·975

These values are plotted in Fig. 1, and between 0° and 1600°, there is the linear relation $C_p=0{\cdot}030725+0{\cdot}0_5 740004\theta$. L. Wöhler and N. Jochum gave for the mol. ht., $c=6{\cdot}156+0{\cdot}002356$. As in the case of platinum and osmium, but unlike ruthenium, rhodium, and palladium, F. M. Jäger observed no sign on the sp. ht. curve of any allotropic change. The at. ht. exceeds the theoretical $3R$ at 40°, at 1600°, C_p is 8·226 Cals., and C_v is 7·840 Cals. E. Grüneisen gave for C_p, 0·0281 from −190° to 17°; and 0·0324 from 17° to 100°. L. Schmitt found the sp. ht. to be 0·0316 for iridium, and the mol. ht. 6·1. A. H. Stuart discussed the relation between the elastic constant and sp. ht.

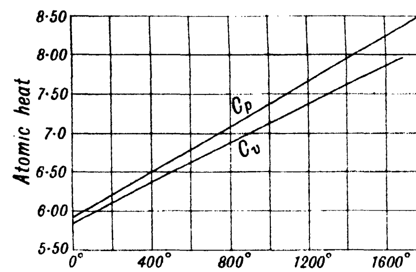

FIG. 1.—The Atomic Heats of Iridium.

J. L. Byers [4] studied the behaviour of the metal on cupellation. J. J. Berzelius was unable to melt iridium in an ether flame fed with oxygen gas; J. G. Children melted it by the electric current; L. N. Vauquelin, by a stream of oxygen on red-hot charcoal; and E. D. Clarke, R. Hare, and R. Bunsen, by the heat of the oxyhydrogen flame. A. Joly and M. Vézes fused the metal in the electric arc furnace in a current of carbon dioxide. There is very little volatilization. The metal is superficially oxidized in air. Lime containers are attacked, and they employed a carbon container. P. H. van der Weyde gave 2200° for the **melting point** of iridium; J. Violle, 1950°; R. Pictet, 2500°; O. Ruff, 2210° to 2225°; O. Ruff and O. Goecke, 2225°; W. Nernst, 2203°, and 2348°; F. E. Carter, 2350°; H. von Wartenberg and co-workers, 2360° when the m.p. of platinum is 1745°—and later he gave for metal of a high degree of purity, 2440° with a possible accuracy of 25°; C. E. Mendenhall and L. R. Ingersoll, 2292° or 2388° according as 1745° or 1789° is accepted for the m.p. of platinum; F. Mylius and R. Dietz, 2360°; W. R. Mott, 2400°; F. Henning and W. Heuse, 2068°; L. Holborn and F. Henning, 2000°; and G. K. Burgess, 2400°; F. E. Carter, 2550°; L. D. Morris and S. R. Scholes, 2454°; F. Henning and H. T. Wensel obtained 2453°, if that of gold be 1063°; and 2455°, if that of platinum be 1773·5°. W. Guertler and M. Pirani, and F. E. Carter considered 2350° to be the best representative value. According to W. Crookes, if the rate of volatilization of platinum at 1300° is 2, that of iridium is 60. For the loss by volatilization in oxygen, etc., *vide infra*. C. E. Mendenhall and L. R. Ingersoll said that the molten metal may be undercooled, and that when the molten metal solidifies there is a momentary flash of light. A. D. van Riemsdijk observed no flashing in cupellation. W. R. Mott estimated 4500° for the **boiling point,** and H. Moissan observed that iridium can be volatilized in the electric arc furnace. F. E. Carter gave 2550° for the b.p. of iridium. W. Crookes found that iridium at 1300° loses 0·828 per cent. in 2 hrs., and 7·297 per cent. in 22 hrs.; and at 900°, 0·030 per cent. in 2·25 hrs., and 0·092 per cent. in 22 hrs. G. W. C. Kaye and D. Ewen studied the disintegration, or

volatilization of iridium under reduced press.; A. Knocke said that in vacuo, an appreciable volatilization occurs at 660°; F. E. Carter, and W. N. Hartley discussed the volatility of iridium—*vide infra*, the action of air; and L. Holborn and L. Austin, the cathodic spluttering in air and hydrogen. J. W. Richards calculated 28 Cals. for the **latent heat of fusion.** G. N. Lewis and co-workers gave 8·7 Cals. for the **entropy** of iridium at 25°; and E. D. Eastman gave 8·7 to 9·3 Cals. The internal energy and entropy were studied by R. von D. Wegener, K. K. Kelley, and W. Herz. J. J. van Laar discussed the **equation of state.**

The **refractive index** of iridium is 4·87 for $\lambda=0·579\mu$; and the **index of absorption,** 2·13. W. W. Coblentz [5] found the **reflecting power,** R, of iridium for light of wave-length, λ, to be:

λ .	1060	3060	5240	6750	9380	12,030
R .	79·4	91·4	94·2	94·7	95·6	96·1 per cent.

The emissivity of the solid is 0·30 for $\lambda=0·65\mu$. The subject was studied by F. Henning, H. von Wartenburg, and L. V. Whitney. A. de Gramont studied the reflection of light by thin films; and G. R. Greenslade, the heat radiation.

W. N. Hartley, and W. N. Hartley and H. Ramage studied the oxyhydrogen **flame spectrum** of iridium. The most intense lines in the visible **spark spectrum** of iridium are 4617 in the blue; 4426, 4400, 4312, and 4268 in the indigo-blue; and 4070, 4020, and 3967 in the violet—Fig. 2—more exactly, 2833·32, 3513·85, 3573·90, 3606·01, 3731·49, 3800·25, 3895·72, 3976·49, 4020·20, 4070·07, and 4399·72. The spark spectrum was studied by G. Kirchhoff, W. A. Miller, R. Thalén, L. de Boisbaudran, G. Kail, W. N. Hartley, F. McClean, H. Nagaoka and co-workers, E. Demarçay, F. Exner and E. Haschek, W. E. Adeney, O. Lohse, and A. Hagenbach and H. Konen; and the under-water spark spectrum, by L. H. G. Clark and E. Cohen, E. O. Hulburt, and W. F. Meggers and O. Laporte. The **arc spectrum** was studied by R. Capron, W. F. Meggers, J. M. Eder and E. Valenta, W. Albertson, H. Kayser, F. Exner and E. Haschek, and A. Hagenbach and H. Konen. The most intense lines are 2924·94, 2943·30, 3100·50, 3220·91, 3266·59, 3368·64, 3449·13, 3513·82, 3516·11, 3522·21, 3573·89, 3638·84, and 3800·25. The **ultra-violet spectrum** was studied by W. A. Miller, G. Kail, A. Miethe and B. Seegert, and F. Exner and E. Haschek; the ultimate rays, by W. N. Hartley and H. W. Moss, and A. de Gramont; and the **Zeeman effect,** by J. E. Purvis. W. Gerlach and co-workers discussed the most sensitive lines for the detection of iridium. J. Formanek observed that aq. soln. of iridium chloride furnish no characteristic **absorption spectrum.** There is some absorption in the blue and violet, and no characteristic reaction with tincture of alkanna. The absorption spectra of salt soln. were studied by R. Samuel and A. R. R. Despande. The **structure** of the spectral lines was studied by W. Albertson, R. de L. Kronig, E. Paulson, W. F. Meggers and O. Laporte, and A. Dauvillier. A. T. Williams discussed the relation between valency and multiple spectra.

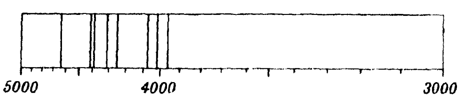

FIG. 2.—The Visible Spark Spectrum of Iridium.

The **X-ray spectrum** was studied by H. G. J. Moseley,[6] J. E. Mack and J. M. Cork, C. del Rosario, E. Friman, J. C. Boyce, W. Stenström, D. Coster, A. Dauvillier, E. Hjalmar, and K. Lang. The K-series of the X-ray spectrum was found by M. Siegbahn, and A. Sommerfeld to exhibit lines corresponding with $\alpha_1\alpha=0·19065$; $\alpha_2\alpha'=0·19550$; $\beta_1\beta=0·16850$; and $\beta_2\gamma=0·16376$, and observations were also made by G. Réchou, J. E. Mack and J. M. Cork, K. Lang, W. Bothe, J. C. Boyce, B. R. Stephenson and J. M. Cork, and J. E. Lilienfeld and H. Seemann. The L-series of the X-ray spectrum was reported by M. Siegbahn, S. Kaufman, K. Lang, S. Idei, R. Ledoux-Lebard and A. Dauvillier, S. K. Allison, and A. Sommerfeld to comprise $\alpha_1\alpha=1·34847$; $\alpha_2\alpha'=1·3598$; $l_\epsilon=1·840$; $L_1=0·9195$;

L_{II}=0·9650 ; L_{III}=1·1036 ; $\beta_1\beta$=1·15540 ; $\beta_2\gamma$=1·13297 ; $\beta_2\phi$=1·1379 ; $\beta_4\phi$=1·1764 ; $\beta_5\zeta$=1·1030 ; $\beta_6\iota$=1·1717 ; β_8=1·1267 ; β_9=1·0874 ; β_{10}=1·10947 ; $\gamma_1\delta$=0·98876 ; $\gamma_2\chi'$=0·9636 ; $\gamma_3\chi$=0·9566 ; $\gamma_4\psi(\psi')$=0·9170 ; $\gamma_5\kappa$=1·0197 ; and $\gamma_6\theta$=0·9636. Observations on the structure of the L-series were also made by E. Hjalmar, J. H. Williams, V. J. Andrew, S. Idei, J. A. Prins and A. J. Takens, A. Sandström, J. Zahradnicek, D. Coster, E. Friman, M. J. Druyvesteyn, A. Dauvillier, P. Augier and A. Dauvillier, M. Siegbahn and E. Friman, R. Ledoux-Lebard and A. Dauvillier, H. Küstner and E. Ahends, and J. M. Cork. The M-series was found by M. Seigbahn, E. Lindberg, J. A. Prins and A. J. Takens, E. G. Purdom and J. M. Cork, and A. Sommerfeld to comprise M_{II}=4·270 ; M_{III}=4·851 ; M_{IV}=5·754 ; M_V=5·961 ; χ=4·548 ; δ=4·769 ; ϵ=6·652 ; γ'=5·528 ; $\gamma\gamma$=5·488 ; ζ=4·858 ; N_{II}–M_{IV}=8·047 ; N_{III}–M_{IV}=7·627 ; $\beta\beta$=6·024 ; N_{III}–M_V=8·000 ; $\alpha_2\alpha'$=6·260 ; $\alpha_1\alpha$=6·248 ; α'=6·213 ; α''=6·230 ; β'=6·008 ; and β''=6·011. Observations on the N-series were made by E. Lindberg, J. A. Prins and A. J. Takens, T. Magnusson, R. A. Rogers, E. Hjalmar, and A. Dauvillier and L. de Broglie.

J. A. Harker and G. W. C. Kaye [7] studied the thermal emission of electrons. The negative current attained with iridium at the m.p. is equivalent to 80 milliamps. C. del Rosario investigated the emission of soft X-rays ; E. Fermi and co-workers, F. H. Newman and H. J. Walke, O. d'Agostino, E. Amaldi and co-workers, L. Sosnowsky, and K. A. Hofmann and co-workers, the induced radioactivity ; F. Rasetti, the emission of γ-rays in the capture of slow neutrons ; J. B. Austin, the characteristic frequency ; T. Pavolini, the photosensitiveness ; and N. Piltschikoff, the Moser rays.

W. Jäger and H. Diesselhorst [8] found the sp. **electrical conductivity** of iridium to be 18·9×10⁴ mhos per cm. cube at 18°, and the temp. coeff. a=0·00411. W. Broniewsky and L. Hackspill gave for the resistance, R,

	100°	0°	−78·3°	−186°
R	8·31	6·10	4·28	1·92

and L. Holborn gave for the temp. coeff. of the resistance, per degree :

	−135°	−39°	50°	150°	250°	350°	450°
100a	0·4110	0·3926	0·3924	0·4012	0·4034	0·4359	0·4393

a subject studied by J. T. MacGregor-Morris and R. P. Hunt, and A. Schulze. W. Meissner and B. Voigt examined the superconductivity of iridium at low temp. G. Braunsfurth investigated the conductivity of thin films ; and F. Simon, and A. T. Waterman, the theory of conductivity.

H. Terrey and H. C. Baker measured the e.m.f. of the cell Hg | Hg_2Cl_2, NaCl | NaCl, Na_2IrCl_6, Na_3IrCl_6 | Ir, and found that the iridi-iridochloride electrode resembles the ferri-ferrochloride electrode, and amounts to about 1·001 volts. C. E. Mendenhall and L. R. Ingersoll found that globules of molten metal in Nernst's filament move with the current. R. H. Atkinson studied the electrolytic transfer of iridium with fused chlorides as electrolytes. P. W. Bridgman observed a relation between the electric resistance R to 30°, 65°, and 95°, and the press., p, up to 12,000 kgrms. per sq. cm. At 30°, $\delta R/R=-(0{\cdot}0_51353-0{\cdot}0_{11}40_p)_p$; at 65°, $\delta R/R=-(0{\cdot}0_5128-0{\cdot}0_{11}39_p)_p$; and at 95°, $\delta R/R=-(0{\cdot}0_5134-0{\cdot}0_{11p})_p$. G. Nordström discussed iridium for resistance wires in electric furnaces ; R. von D. Wegener, the contact electricity.

E. G. Weischede [9] found that a soln. of sodium chloroiridate with 17·6 grms. of iridium in 100 c.c., acidified with a few drops of sulphuric acid, has an electrode potential of 0·702 volt at 20°, and 0·0723 volt at 60° ; in the electrodeposition of iridium, the deposition potential was 0·11 to −0·12 volt at 20° and 0·22 to −0·08 volt at 60° when the current densities were respectively 2×10^{-4} and 5×10^{-4} amp. per sq. cm. H. Terrey and H. C. Baker studied the e.m.f. of the cell Hg : $HgCl_2$ +N-NaCl+Na_2IrCl_6+Na_3IrCl_6 : Ir ; and J. A. V. Butler and co-workers, the oxidation potential. E. Newbery observed the anodic overvoltage of iridium in

acid is nearly constant at 0·50 volt. The electrodeposition of iridium was studied by I. I. Tschukoff, and L. Schurcht; and R. H. Atkinson, from soln. of K_2IrCl_6 in fused alkali chlorides. R. Luther and F. J. Brislee observed that iridium anodes in the electrolysis of hydrochloric acid do not exhibit the passive phenomena shown by platinum anodes. A. D. Garrison and J. F. Lilley studied the oxygen overvoltage; and A. Thiel and W. Hammerschmidt, the hydrogen overvoltage. S. C. Woo measured the electromotive force of the cell $Ir \mid IrCl_6{}''', IrCl_6{}'', N\text{-}HCl \mid N\text{-}HCl \mid H_2(Pt)$—one atm. at 20° and 25°, and obtained −1·0313 and −1·0264 volts respectively when the conc. of the Ir salts is between 0·002 and 0·008. The reduction potential of the reaction $IrCl_6{}'''+N\text{-}HCl=IrCl_6{}''+N\text{-}HCl+\ominus$ is 1·021 at 25° referred to the normal hydrogen electrode. The corresponding changes of free energy, and heat content are respectively −23·54 Cals., and −30·4 Cals. J. A. V. Butler and G. Drever observed that when iridium electrodes are anodically polarized in acidic or alkaline soln., an adsorbed layer of oxygen is formed prior to the establishment of the oxygen overvoltage. No peroxidation was observed. A. D. Garrison and J. F. Lilley studied the oxygen overvoltages on iridium; S. Koidzumi, the anodic behaviour in alkaline soln.; and S. C. Woo and D. M. Yost, the electrometric titration of the chloroiridate by titanous chloride. S. Girgoloff and J. Schukoff recommended the use of iridium electrodes in determinations of H˙-ion concentrations.

E. O. Hulburt[10] studied the **cathode spluttering** of iridium; and L. Tonks, the anchoring of the cathode spot. Drops of molten tellurium dioxide were found by A. Simek not to move on hot iridium as they do on platinum.

L. Holborn and A. L. Day[11] found the **thermoelectric force,** E millivolts, for the iridium-platinum couple:

	−185°	−80°	0°	100°	300°	500°	700°	900°	1100°	1300°	1500°
E .	−0·28	−0·32	0	0·65	2·47	4·78	7·56	10·80	14·48	18·47	22·50

W. Broniewsky and L. Hackspill gave 0·68 millivolt for the iridium-platinum thermocouple at 100°; or from −78° to 100°, $E=2{\cdot}44-0{\cdot}0014\theta$. O. Feussner studied the thermoelectric force of iridium against an alloy of iridium with 60 per cent. of rhodium, and showed that it can be used for thermocouples up to 2000°. J. Monheim studied the iridium-copper couple.

H. B. Peacock observed that with thin films of iridium at 18°, **Hall's effect** is 34×10^{-6}; and H. Zahn gave 402×10^{-6} at 20°; H. Zahn found **Ettinghausen's effect** to be very small; **Nernst's effect,** -5×10^{-6}; and **Leduc's effect,** 55×10^{-9}.

L. Holborn and L. Austin,[12] and F. Rother studied the cathodic spluttering of iridium. If the rate for platinum be 40, that for iridium is 10.

M. Faraday[13] found iridium to be diamagnetic. K. Honda observed the **magnetic susceptibility** to be $0{\cdot}15\times10^{-6}$ mass unit at 18°, and $0{\cdot}3\times10^{-6}$ mass unit at 1100°; and M. Owen gave $0{\cdot}129\times10^{-6}$ mass unit. A. N. Guthrie and L. T. Bourland found that the paramagnetic susceptibility increases with temp. up to 427°. B. Cabrera and A. Dupérier gave $Ir^{\cdots}=+47{\cdot}2\times10^{-6}$ c.g.s. unit. W. Finke observed $4{\cdot}89\times10^{-6}$ vol. unit.

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§ 4. The Chemical Properties of Iridium

F. Fischer and F. Schröter [1] observed no sign of chemical combination when iridium is electrically spluttered in liquid **argon.** L. P. Cailletet and E. Collardeau observed that if a current be passed through electrodes of spongy iridium in dil. sulphuric acid, until both electrodes are saturated with gases, and the two electrodes then placed in electrical communication, a kind of gas battery is formed. Under atm. press., the discharge lasts about 10 seconds, and the e.m.f. falls to zero. The duration of the current is increased by press. The subject was discussed by M. Berthelot.

T. Wilm observed that spongy iridium absorbs **hydrogen,** and the hydrogenized spongy metal glows on exposure to air as the absorbed gas is oxidized to water. According to F. Rother, when iridium foil is subjected to long-continued cathodic pulverization in vacuo, it becomes capable of absorbing at the ordinary temp. about 800 times its vol. of hydrogen. The structure of the plate is apparently much altered; and it appears dull grey and brittle, and the vacuum is increased by the absorption of hydrogen into the iridium cathode surface. The absorption of hydrogen can readily produce an explosion, but the introduction of nitrogen moderates the pulverization. A. Gutbier and co-workers measured the absorption of hydrogen by purified iridium sponge, between —30° and 100°. Some results are indicated in Fig. 3. The curve showing the vol. of hydrogen absorbed per unit vol. of metal has a minimum at about 0°, and a maximum at about 20°. A. Gutbier and W. Schieferdecker found that the isobars with iridium-black are nearly straight

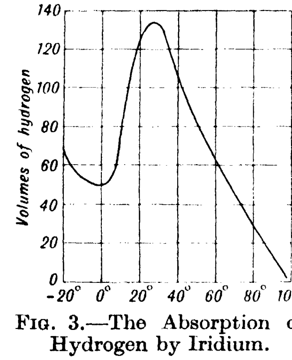

FIG. 3.—The Absorption of Hydrogen by Iridium.

lines of negative slope; the absorptive power of the metal is diminished by strong ignition, but by a prolonged heating not above 350°, its absorptive power for low temp. is increased. Very little gas is removed at 18° in vacuo, but at 50° nearly all is driven off. E. Müller and K. Schwabe observed that all the hydrogen taken up by reduced iridium is irreversibly absorbed, indicating chemical combination. I. I. Tschukoff considered that no *iridium hydride* is formed. The catalytic action of iridium in the oxidation of hydrogen was studied by K. A. Hofmann.

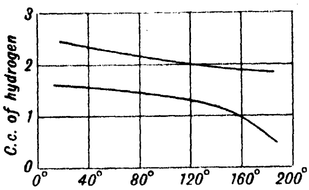

FIG. 4.—Isobars of the System: Ir–H_2.

J. J. Berzelius said that when iridium, not in a compact state, is ignited in **air**, it is oxidized to the sesquioxide. According to L. Holborn and co-workers, the loss in weight which occurs when iridium is heated in hydrogen is so small that it may be due to the presence of traces of **oxygen** in the gas. W. Crookes observed the following losses when iridium is heated in air:

Time	2	6	10	14	18	22 hrs.
Loss 1300° . .	0·828	2·414	3·686	4·887	5·884	7·297 per cent.
Loss 900° . .	0·030	0·048	0·074	0·076	0·088	0·092 ,,

The volatility of iridium was observed by W. N. Hartley. F. E. Carter found that oxidation to the dioxide begins at about 800°, and it volatilizes freely as oxide at 1000°. J. H. T. Roberts showed that the rate of loss of weight with iridium is much greater than it is with platinum and rhodium, and is practically zero when oxygen is absent—say, in vacuo. If oxygen is present, the rate of loss of weight diminishes with a fall in the press. of oxygen, so that the phenomenon is connected with the formation and decomposition of a volatile oxide. F. Emich also observed no loss in non-oxidizing gases, and he assumed that the loss in weight is due to the formation of an oxide volatile at a high temp. L. Wöhler and W. Witzmann observed that iridium is most rapidly oxidized to the dioxide at 1070°. A gram of iridium in oxygen at 775° loses 0·33 mgrm. per hour, and at 1000°, about 0·5 mgrm. per hour. The volatile substance is possibly a tetroxide which is endothermic, and decomposes on cooling, forming the dioxide. T. Wilm thought that a suboxide is formed when iridium is heated in air or oxygen to dull redness; and J. J. Berzelius, that the hemitrioxide is formed, and reduced at a higher temp. C. Claus, however, showed that the hemitrioxide is not formed under these conditions; and L. Wöhler and W. Witzmann, that the dioxide is formed when finely divided iridium is heated to bright redness in air or oxygen. The observed products are assumed to be incompletely oxidized mixtures of iridium and of its dioxide. G. Geisenheimer found that the reaction is very slow. A. Gutbier and co-workers, K. A. Hofmann, F. Rother, F. C. Phillips, and T. Wilm observed that iridium, like platinum (*q.v.*) acts catalytically on the union of hydrogen and oxygen, and with spluttered iridium in electrolytic gas, an explosion ensues. F. C. Phillips placed the metals in the order of their catalytic activities, Os, Pd, Pt, and Ir, in oxidizing hydrogen; and H. Remy and co-workers gave Ir, Pd, and Pt, whilst the other three platinum metals were inactive. L. P. Hammett and A. E. Lorch studied the activation of hydrogen by iridium; and H. Remy and H. Gonnington, the hydrogen-oxygen reaction.

C. F. Schönbein observed that iridium hastens the conversion of **ozone** into oxygen. F. Emich found that iridium loses weight when heated in **water** vapour, owing, it is assumed, to the formation of a volatile higher oxide. The speed of the reaction is greater as the press. falls from 1·0 to 0·1 atm. G. A. Brossa, I. I. Shukoff and co-workers, and G. Kernot and F. Arena studied the acceleration in the rate of decomposition of **hydrogen dioxide** by colloidal iridium. As in the corresponding case with platinum (*q.v.*), the reaction is unimolecular, and the speed of the reaction

is approximately proportional to the concentration of the catalyst. The speed of the reaction is not affected by alkalies, it is accelerated by dil. acids, and it is retarded or inhibited by hydrogen sulphide, mercuric chloride or cyanide, and potassium cyanide, but not by iodine. C. Paal and C. Amberger placed the activity of the colloidal metals on the decomposition of hydrogen dioxide in the order: Os, Pd, Pt, and Ir. G. R. Levi studied the subject. E. Leidié and L. Quennessen found that when iridium is heated with **sodium dioxide,** there is formed a soluble iridate, K. A. Hofmann and O. Schneider found that the catalytic activity of the platinum metals in oxidizing hydrogen in the presence of sodium chlorate decreases in the order, Pt, Rh, Ru, Pd, Au, Os, Ir, Ag.

H. Moissan observed that **fluorine** does not attack iridium in the cold, but at a dull red-heat, the attack is vigorous, and fumes of iridium fluoride are given off; and O. Ruff also observed the attack by fluorine at a dull red-heat. H. Moissan also found that an iridium anode is rapidly corroded in the electrolytic process for fluorine. J. J. Berzelius, U. Antony, and C. Claus observed that iridium is attacked by **chlorine** at a dull red-heat, forming the trichloride, but, according to U. Antony, a mixture of chlorine and carbon monoxide does not attack iridium at 245°, although platinum is attacked under these conditions. In the presence of sodium chloride at a dull red-heat, iridium is completely converted by chlorine into sodium chloroiridate. C. F. Schönbein observed that iridium black converts a mixture of oxygen and chlorine water into oxygen and hydrochloric acid. O. Ruff and H. Krug observed that **chlorine trifluoride** reacts with iridium with incandescence. According to C. Birnbaum, iridium at a dull red-heat is slightly attacked by **bromine,** in the presence of an alkali bromide, and, according to T. Oppler, by **iodine.** Iridium is not attacked by **hydrochloric acid** in the absence of air, but T. Wilm, and A. M. Vasileff showed that iridium is attacked without the evolution of hydrogen if it be allowed to stand in contact with hydrochloric acid exposed to air; and C. Matignon observed that it is dissolved when heated at 125° in a sealed tube with hydrochloric acid and oxygen. C. F. Schönbein observed that **hypochlorites** are converted into chlorides in the presence of iridium black.

According to J. J. Berzelius, iridium at a red-heat unites with **sulphur** vapour with a slight incandescence, incompletely forming a sulphide. W. Crookes observed that sulphur in coal gas has no perceptible effect on iridium crucibles. G. R. Levi and M. Faldini found that iridium lowers the catalytic activity of platinum catalysts in the oxidation of **sulphur dioxide,** owing, said S. Pastorello, to the formation of iridium sesquioxide. According to J. J. Berzelius, purified iridium does not dissolve in **sulphuric acid.** F. Emich observed no loss in weight occurs when iridium is heated to 1500° to 2150° in **nitrogen** free from oxygen, but there is a marked loss in nitrogen containing a little oxygen—say, 2·2 per cent. F. Becker observed no adsorption of nitrogen occurs when finely-divided iridium oxidizes in air between 900° and 1040°. J. J. Berzelius found that purified iridium does not dissolve in **nitric acid,** and that it is very slightly attacked by **aqua regia.** S. J. Green studied the reduction of nitro-compounds with iridium as catalyst. W. Crookes observed that boiling aqua regia has no perceptible effect on iridium crucibles. J. J. Berzelius prepared iridium-black which is soluble in aqua regia; and the iridium in an iridium-platinum alloy dissolves freely in aqua regia. J. J. Berzelius found that when iridium is heated to redness in the vapour of **phosphorus,** an impure phosphide is formed. L. Duparc and co-workers studied the oxidation of **ammonia** with an iridium catalyst; and also the hydrogenation of **nitrous oxide.** An alloy of iridium or osmiridium with phosphorus, described by F. W. Clarke and O. T. Joslin, is used in place of osmiridium for pen-points. W. Crookes observed that fused **phosphates**—*e.g.*, microcosmic salt—with frequent additions of carbon have no perceptible effect on iridium crucibles. G. Geisenheimer observed that **phosphorus pentachloride** has no action on iridium; but W. Strecker and M. F. Schurigen, and M. F. Schurigen observed that when iridium sponge is heated with phosphorus

pentachloride at 300°, some $IrCl_3.3PCl_3$ is formed; and similarly with **phosphorus pentabromide.**

J. J. Berzelius observed that a coherent piece of iridium held in the middle of an alcohol flame soon becomes covered with a carbonaceous "vegetation," which is soft to the touch, stains the fingers, and takes fire when slightly heated, and afterwards continues to glow. The iridium on which this carbonaceous mass has been deposited appears dark grey, and is completely penetrated by the **carbon.** On the other hand, W. Crookes found that when an iridium crucible is heated for some hours in the bunsen flame, with an insufficient supply of air, the crucible is not harmed when the deposit of carbon is burnt entirely away. H. Moissan found that molten iridium dissolves carbon, but on cooling the carbon separates out as graphite. H. Wölbling studied the adsorption of iridium by active carbon. J. Gerum observed how **carbon monoxide** is oxidized in the presence of colloidal iridium. K. A. Hofmann and O. Schneider found that the catalytic activity of the platinum metals in oxidizing carbon monoxide in the presence of sodium chlorate, decreases in the order Os, Rh, Au, Pt, Ru, Pd, Ir, Ag. A. Gutbier and W. Schieferdecker found the isobars for the absorption of carbon monoxide by iridium black, Fig. 5, are similar to those of the iridium-hydrogen system, and by heating the metal for a prolonged period in an atm. of carbon monoxide, the absorptive power at low temp. is considerably increased. F. Fischer and co-workers compared the catalytic activity of the platinum metals in reducing carbon monoxide to methane. F. Emich observed that when iridium is heated to 1500° to 2150° in an atm. of carbon monoxide, no loss in weight is perceptible, but in an atm. of **carbon dioxide,** a marked loss occurs owing to the formation of a volatile oxide—possibly a tetroxide—during the dissociation of the carbon dioxide. The speed of the reaction is reduced as the press. falls from 1·0 to 0·25 atm., and then is increased if the press. is lowered still more. C. Paal observed that at ordinary temp. colloidal iridium converts carbon monoxide and oxygen into carbon dioxide. F. Mylius and C. Hüttner found that iridium powder gently heated in a current of coal gas saturated with **carbon disulphide** forms a black mass containing carbon and sulphur. F. C. Phillips observed that iridium asbestos favours the oxidation of **hydrocarbons.** C. Paal and A. Schwarz studied the adsorption of **acetylene** by colloidal iridium; and they found that the hydrogenation of acetylene is not influenced by colloidal iridium; and C. Paal and J. Gerum examined the effect of colloidal iridium on the hydrogenation of nitrobenzene; N. D. Zelinsky and M. B. T. Pollak, of benzene; J. W. Döbereiner observed that in the presence of iridium black, in air, **alcohol** is converted into acetic acid as in the analogous case with platinum black (*q.v.*). When iridium black is placed on paper moistened with alcohol, there is a hissing noise, the iridium black becomes red-hot and acquires the grey colour of ignited iridium. R. Böttger made observations on the subject. H. St. C. Deville and H. Debray, and E. Müller and co-workers studied the catalytic decomposition of **formic** acid; and F. Plzak and B. Husek, the hydrolysis of **sugar.**

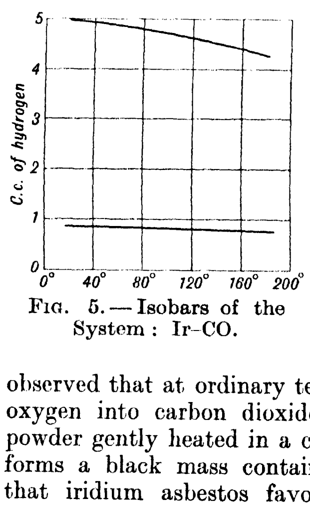

FIG. 5.—Isobars of the System: Ir–CO.

W. Crookes observed that iridium crucibles are not perceptibly attacked when heated with **silica** or **silicates** along with a reducing agent. A prolonged heating of an iridium crucible with **copper** renders the crucible brittle when hot, but the copper can be burnt off; molten **gold** has no perceptible effect. Boiling **zinc** has no perceptible action on an iridium crucible, and zinc, run in with acid zinc chloride and heated to boiling, attacks the crucible only superficially; boiling **lead** at a white-heat has no perceptible action on an iridium crucible; and no attack was observed with molten **iron,** or molten **nickel.** F. Wever examined the effect of iridium on

the transformation points of iron. The iridium steels of J. Stodart and M. Faraday were studied by R. A. Hadfield. H. Remy and B. Schäffer found that the **ruthenium-iridium alloy** is more active than either metal alone as a catalyst in the reaction between hydrogen and oxygen. F. E. Carter said that **iridium-osmium alloys** occur in nature, and both the natural and artificial alloys are used for tips for fountain pens. J. J. Berzeluis observed that molten **potassium hydroxide** to which air has access, or potassium hydroxide mixed with nitre, oxidizes iridium—*vide supra*, opening up native osmiridium. W. Crookes added that fused potassium hydroxide attacks iridium less than it does platinum. J. J. Berzelius observed that molten potassium hydrosulphate converts iridium into an insoluble oxide. E. Tiede and R. Piwonka studied the iridium **alumina** phosphors. H. Weisz observed that iridium can serve as nuclei in the solarization of **silver bromide** films.

Some reactions of analytical interest.—When a soln. of sodium chloroiridate or iridium chloride is treated with **hydrogen sulphide,** the soln. is decolorized, and brown iridium hemitrisulphide is precipitated. The precipitate is also produced by **ammonium sulphide,** and it is soluble in an excess of that reagent. When **sodium hydroxide** is added, the colour changes from dark red to green, and on warming it becomes reddish and finally azure blue; and a similar coloration is obtained with **sodium hypochlorite** or **hypobromite**—according to F. Mylius and A. Mazzucchelli,[2] this is a very characteristic reaction—if the soln. be now acidified with hydrochloric acid, treated with a little alcohol to destroy the hypochlorite, and then with potassium chloride, no precipitation occurs because the K_3IrCl_6 which is formed is freely soluble in water—not as with the corresponding platinum salt. A sparingly soluble, brownish-black potassium chloroiridate is precipitated when **potassium chloride** is added to the soln.; it is insoluble in a soln. of potassium chloride, and in alcohol; **ammonium chloride** gives an analogous dark red precipitate. O. W. Gibbs noted that **potassium nitrite** reduces the chloroiridate, forming an olive-green liquid, which becomes yellow when boiled, and deposits $K_3IrCl_6.3K_3Ir(NO_2)_6$, as a yellowish-white precipitate sparingly soluble in hydrochloric acid or in boiling water. The reaction can be employed to separate iridium from platinum. M. C. Lea found that **oxalic acid** reduces the soln. to the lower chloride; and reduction to the lower chloride occurs with **ferrous sulphate, stannous chloride, sulphurous acid, alcohol, hydrogen dioxide,** and **alkali** (L. Vanino and L. Seeman), and **hydroxylamine** (P. Jannasch and O. von Mayer)—reactions which enable iridium to be separated from gold. Soln. of iridium salts are reduced to metal by **formic acid,** or **zinc**—L. Quennessen said that **magnesium** gives a precipitate of what is probably an oxide which becomes blue at 100°. O. Makowka observed that unlike palladium, acetylene gives no precipitate with soln. of iridium salts. C. Birnbaum observed that if iridium oxide be suspended in a soln. of **potassium sulphite,** saturated with sulphur dioxide, and boiled with a renewal of water until all the sulphur dioxide is expelled, the iridium forms an insoluble sulphite; and the platinum sulphite remains in soln. A deep blue colour is obtained by warming an iridium salt soln. with **aniline sulphate** (S. C. Ogburn). V. G. Chlopin said that quadrivalent iridium gives a sky-blue coloration with **benzidine;** and tervalent iridium a green colour; J. H. Yoe, a red solution with **ammonium aurintricarboxylate;** W. N. Ivanoff obtained an incomplete precipitation with **sodium thiocyanate.** W. Singleton recommended as tests the reaction with sodium thiocyanate and ammonium nitrate soln., and the formation of reddish-brown crystals with hexamethylene tetramine. O. Makowka found that iridium salt soln. do not precipitate iridium with **acetylene.**

Some uses of iridium.—Iridium alone is difficult to work mechanically. W. Crookes[3] discussed the characteristics of iridium crucibles. Alloys with platinum are employed where platinum alone is not hard enough—pivots, surgical tools, the metric and kilogram standards. F. Förster recommended the alloy as an electrode in preparing chlorates; R. J. Gülcher, as a filament for incandescent lamps; and G. F. C. Frick, as a black pigment for porcelain painting.

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§ 5. The Atomic Weight and Valency of Iridium

The atomic weight of iridium is about 193. According to S. Streicher,[1] and L. Wöhler and S. Streicher, iridium exists as a univalent element in the monochloride, IrCl. L. Wöhler and W. Witzmann question the existence of *bivalent* iridium in the doubtful monoxide, IrO, but other compounds of the bivalent element are known—*e.g.* the iridium dichloride of S. Streicher, and L. Wöhler and S. Streicher. Iridium is *tervalent*, in the sesquioxide, Ir_2O_3, and the trichloride, $IrCl_3$, as in the analogous salts of iron, and aluminium, and in its compounds with the metal chlorides, $3KCl.IrCl_3$; *quadrivalent* in the dioxide, IrO_2, the tetrachloride, $IrCl_4$, and in compounds of the tetrachloride with the metal chlorides—$2KCl.IrCl_4$; *quinquevalent* in O. Ruff and J. Fischer's iridium pentafluoride, IrF_5; and *sexivalent* in L. Wöhler and W. Witzmann's iridium trioxide, IrO_3, and in O. Ruff and J. Fischer's hexafluoride, IrF_6. T. M. Lowry, and A. T. Williams discussed the subject; M. Gerber, some relations of the at. wts.; and A. Werner and co-workers, M. Delépine, F. M. Jäger, and C. E. Wood and S. D. Nicolas, the stereochemistry of the iridium salts.

The value 193 for the at. wt. of iridium is in approximate harmony with the sp. ht. rule; with the isomorphous rule exemplified by the alums; and with the analogies with the platinum metals and its position in the periodic table between osmium and platinum.

In 1826, T. Thomson [2] attempted to obtain a value for the at. wt. of iridium, and in 1828, J. J. Berzelius calculated the at. wt. of iridium from the analysis of potassium chloroiridate to be 196·7. This result was generally accepted for nearly half a century. In 1878, K. Seubert calculated 193·38 from the ratio $(NH_4)_2IrCl_6 : Ir$; 192·99 from the ratio $K_2IrCl_6 : Ir$; 192·88 from the ratio $K_2IrCl_6 : 2KCl$; and 193·26 from the ratio $K_2IrCl_6 : 4Cl$. A. Joly obtained 193·07 from the per cent. of potassium chloride in the salt K_3IrCl_6, and 193·27 from the per cent. of iridium in $(NH_4)_2IrCl_6$. D. Hoyermann obtained 192·59 from the ratio $(NH_4)_2IrCl_6 : Ir$, and F. Holzmann, 193·40 from the same ratio. E. H. Archibald obtained 192·9 from the analysis of potassium chloroiridate. F. W. Clarke gave 193·047 for the best representative value; and the International Table gave 193·1.

The **atomic number** of iridium is 77. F. W. Aston [3] observed no **isotopes,** but B. Venkatesachar and L. Sibaiya gave 191 and 193 in the relative proportions of 1 : 2. O. d'Agostino obtained an isotope of iridium as a product of induced radioactivity. Neither E. Rutherford and J. Chadwick, nor H. Pettersson and G. Kirsch have observed the **atomic disruption** of iridium by its bombardment with α-rays. The **electronic structure,** according to N. Bohr, and E. C. Stoner, is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 4, 6) for the M-shell; (2, 2, 4, 4, 6, 6, 8) for the N-shell; (2, 2, 4, 4, 3) for the O-shell; and (2) for the P-shell—or else (2, 2, 4, 4, 4) for the O-shell, and (1) for the P-shell. The subject was studied by F. D. Foote, S. K. Allison, H. J. Walke, C. D. Niven, H. Schüler and T. Schmidt, and S. Kato.

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§ 6. The Alloys and Intermetallic Compounds of Iridium

P. G. Ehrhardt [1] observed that a **lithium-iridium alloy** is harder than iridium alone. L. N. Vauquelin observed a **copper-iridium alloy** which was fairly ductile, and harder than copper; nitric acid extracts the copper from the alloy. L. N. Vauquelin, and S. Tennant obtained a malleable **silver-iridium alloy.** H. Rössler said that iridium does not alloy with silver. W. Truthe studied the behaviour of the alloy on cupellation. S. Tennant prepared a malleable **gold-iridium alloy** resembling gold in colour, and aqua regia extracts the gold and leaves the iridium behind. W. Mietschke noted the segregation of the molten alloy.

H. St. C. Deville and H. Debray obtained a **zinc-iridium alloy.** R. Böttger obtained **iridium amalgam,** or **mercury-iridium alloy,** not by direct union, but by the action of sodium amalgam on an aq. soln. of sodium chloroiridate. When ignited some mercury remains in the residue, and it can be extracted with nitric acid. The residual iridium is soluble in aqua regia. F. Rother obtained the amalgam by triturating hydrogenized, cathodically-spluttered iridium with mercury.

L. N. Vauquelin prepared a dull white, crystalline, hard, malleable **tin-iridium alloy,** and H. Debray, and H. St. C. Deville and H. Debray observed the presence of cubic crystals of **iridium distannide,** $IrSn_2$, which can be isolated by removing the excess of tin with hydrochloric acid. L. N. Vauquelin prepared a ductile **lead-iridium alloy** which is harder than lead, and when treated with nitric acid, leaves the iridium as a black powder. F. Mylius and O. Fromm precipitated the alloy by the action of lead on a soln. of an iridium salt. S. Tennant found that the lead could be also removed by cupellation. H. St. C. Deville and H. Debray observed that no compound is formed as in the case of the tin alloy. E. Friederich observed that the **iridium-chromium alloy** with 10 per cent. of chromium is ferro-magnetic. F. Beck studied the etching of the **iridium-rhenium alloys.**

J. J. Berzelius obtained a black precipitate on adding iron to a soln. of iridium sulphate, and the precipitate contained both iron and iridium. J. Stodart and M. Faraday obtained an **iron-iridium alloy,** in which the iron is hardened; these alloys were also studied by R. A. Hadfield, and P. Oberhoffer. J. B. J. D. Boussingault said that the hardening effect was due to the presence of carbon. H. St. C. Deville also prepared some alloys. H. Remy and H. Gonnington studied the catalytic effect on the hydrogen-oxygen reaction; and similarly with the **cobalt-iridium alloy** and the **nickel-iridium alloy.**

H. St. C. Deville and H. Debray [2] prepared a **ruthenium-iridium alloy** by melting the two metals together; and A. Schulze, O. Feussner, and C. W. Waidner and G. K. Burgess studied the thermoelectric force of a couple of iridium-ruthenium against iridium. H. Remy and H. Gonnington studied the catalysis on the hydrogen-oxygen reaction. O. Feussner, and A. Schulze studied the thermoelectric force of the **iridium-rhodium alloy** against iridium, and employed the thermocouple

up to 2000°. H. Remy and H. Gonnington studied the catalytic effect on the hydrogen-oxygen reaction. The **osmium-iridium alloys** occurring native have been discussed in connection with the occurrence of platinum. J. Beckenkamp found that iridosmium is a solid soln. of the two metals with a lattice of the magnesium type. These alloys are very hard, and are used on pen points, and as alloys for special ignition work where hardness and high fusion temp. are required. F. C. Carter noted that iridium does not harden palladium to the same extent as it does platinum; and that **palladium-iridium alloys** with over 20 per cent. of iridium can be worked only with great difficulty. The Brinell's hardness, H, and the electrical resistance, R ohms per million ft., are:

Iridium	5	10	15	20 per cent.
H Hard	107	130	—	—
H Annealed	62	81	110	152
R	86	123	210	235

The palladium-iridium alloys were studied by A. W. Smith. F. A. Genth, B. Silliman, and J. D. Dana described its occurrence in California; T. L. Gledhill, in British Columbia; T. S. Hunt, in Canada; N. von Kokscharoff, J. J. Berzelius, G. Rose, P. Groth, K. Zerrenner, and A. von Lasaulx, in Russia; L. Horner, in Borneo; G. H. F. Ulrich, in Victoria; A. Liversidge, and J. C. H. Mingaye, in New South Wales. The mineral also occurs in the platinum ores (*q.v.*) of Colombia, and Brazil in South America. Analyses were reported by C. Claus, H. St. C. Deville and H. Debray, and J. J. Berzelius. J. J. Berzelius represented his results by formulæ, IrOs, $IrOs_3$, and $IrOs_4$ but there is nothing to confirm the existence of definite osmides. Some other metals—platinum, ruthenium, rhodium, copper, and iron –are usually present. F. Wöhler found gold in some varieties. H. Debray obtained alloys of the two metals.

The early mineralogists regarded the mineral as an alloy of osmium and iridium in accord with the analysis of S. Tennant, and W. H. Wollaston. K. C. Leonhard called it *osmium-iridium;* A. Breithaupt, *iridosmine;* E. F. Glöcker, *osmiridium* or *iridosmium*, according to the relative proportions of the two elements—*vide* occurrence of platinum; and W. Haidinger called osmiridium *sysserekite*, and iridosmium, *nevyanskite* after localities in the Urals.

The colour of the mineral is tin-white to light steel-grey. The mineral usually occurs in irregular, flattened grains, rarely in hexagonal prisms. G. Rose showed that the rhombohedral crystals have the axial ratio $a:c=1:1{\cdot}4105$; and T. L. Gledhill gave $1:1{\cdot}3823$. The (0001)-cleavage is perfect. The two varieties are isomorphous, and the solid soln. contain different proportions of the two metals. The crystals were examined by H. Zenger, K. Zerrenner, P. Groth, A. von Lasaulx, J. L. de Bournon, T. L. Gledhill, and P. von Jeremejeff. G. Aminoff and G. Phragmen found the X-radiograms of a specimen of sp. gr. 19·0 correspond with a hexagonal cell with the parameters $a=2{\cdot}90$ A., and $c=4{\cdot}60$ A. O. E. Swjaginzeff and B. K. Brunowsky regarded osmiridium as a solid soln. of iridium (platinum) and osmium: and for samples with Os+Ru=44·3, 64·3, and 100 per cent., and Ir+Pt+Rh, respectively, 50·9, 31·9, and 0, a was respectively 2·620, 2·710, and 2·716 A.; c, respectively, 4·235, 4·282, and 4·331 A.; and $a:c=1:1{\cdot}617$, $1:1{\cdot}581$, and $1:1{\cdot}595$. Values for the sp. gr. by G. Rose, and J. J. Berzelius range from 18·645 to 21·118; and the hardness from 6 to 7. O. E. Swjaginzeff found that the sp. gr. varies with the ruthenium content, and with the proportion of contained ruthenium. The mineral is slightly malleable, but brittle. When heated, the smell of osmium can be detected. H. Remy and H. Gonnington studied the catalytic effect in the hydrogen-oxygen reaction. The mineral is insoluble in aqua regia. C. Claus opened up the mineral by fusion with potassium hydroxide and nitrate—*vide* the extraction of osmium. F. von Kobell said that when dipped with zinc pincers in a soln. of copper sulphate, the mineral acquires a film of copper. S. Tennant, and J. J. Berzelius said that no definite compound is obtained when

osmiridium is fused with copper, silver, gold, zinc, tin, lead, or bismuth. J. Stodart and M. Faraday said that osmiridium unites in all proportions by fusion with steel, and they examined the properties of some alloys. P. O. Lemon discussed the uses of the alloy for pen nibs.

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§ 7. The Oxides of Iridium

According to J. J. Berzelius,[1] when iridium dichloride is boiled with potash lye, and the heavy black powder which separates is washed with dil. acid, and water to free it from alkali, there remains **iridous oxide,** or **iridium monoxide,** IrO. This oxide is also produced by the ignition of **iridous hydroxide,** or **iridium hydroxide,** $Ir(OH)_2$, which is formed when an aq. soln. of iridium dichloride is treated with alkali carbonate, in slight excess. The potash lye filtered from the iridium monoxide retains some iridium in soln., and when exposed to air, it gradually absorbs oxygen, forming first a purple-red, and then a dark blue soln.

The blue soln. is also produced by the partial deoxidation of soln. of the sesquioxide. The *blue iridium oxide* was considered by J. J. Berzelius to be a mixture of the monoxide and sesquioxide ; and C. Claus showed that it is probably the hydrated dioxide—*vide infra.* L. N. Vauquelin made some observations on the blue soln. C. Claus, and K. Seubert obtained what they regarded as the monoxide by heating a chloroiridate with an alkali hydrosulphite: but L. Wöhler and W. Witzmann could not prepare the monoxide by the decomposition of a complex sulphite, $R_2SO_3.IrSO_3.nH_2O$, with alkali, or by any other means ; they also said that the dissociation press. of the hydrate is too great for it to exist at ordinary temp. W. Palmaer made unsuccessful attempts to prepare **iridous diamminohydroxide,** $[Ir(NH_3)_2(OH)_2]$, and **iridous tetramminohydroxide,** $[Ir(NH_3)_4](OH)_2$. According to J. J. Berzelius, when iridium dichloride is boiled with potash lye, part of the resulting iridium monoxide remains in soln. as **potassium iridite ;** and similarly with potassium carbonate. The soln. becomes purple and then blue on exposure to air.

J. J. Berzelius reported that finely-divided iridium is quickly converted into **iridium sesquioxide,** or **iridium hemitrioxide,** Ir_2O_3, when ignited in air, but the compact metal is oxidized more slowly. At a higher temp., the oxide is decomposed and resolved into the metal. H. St. C. Deville and H. Debray found that above 1139°, the dissociation press. of the oxide exceeds 1 atm., so that the oxide is not formed at temp. exceeding 1139°. T. Wilm's product, with the composition $Ir_2O.IrO$, or Ir_3O_2, was probably a mixture of oxide and metal. W. Witzmann, and L. Wöhler and W. Witzmann found that the hemitrioxide decomposes into the dioxide and iridium about 400°, so that it is very doubtful if the alleged hemitrioxide is not a mixture of the dioxide and the metal. J. J. Berzelius said that the sesquioxide is formed when iridium is heated with potassium hydroxide, or carbonate, or with potassium hydrosulphate while exposed to air ; and that the same oxide is also formed when iridium is heated with a mixture of potassium hydroxide and nitrate. J. J. Berzelius also prepared the hemitrioxide by heating to dull redness a mixture of potassium chloroperiridite and alkali carbonate. If the temp. be raised too high, the sesquioxide unites with the alkali to form a compound which dissolves in water with a yellow soln. The product is digested with boiling water, and the sesquioxide is collected on a filter, washed with water containing ammonium chloride, for if water alone is employed, a greenish-blue colloidal soln. is formed, and the adherent ammonium chloride removed by heat. Any adherent alkali is then removed by washing with water. C. Claus obtained the hemitrioxide by igniting iridium sulphite. L. Wöhler and W. Witzmann, and W. Witzmann obtained an impure hemitrioxide by mixing hot, air-free soln. of potassium hydroxide and sodium chloroperiridite in an atm. of carbon dioxide ; evaporating the soln. to dryness, and heating the residue to redness in an atm. of carbon dioxide. The product is boiled with a soln. of sodium hydroxide, and then with sulphuric acid. According to L. Wöhler and W. Witzmann, when the hemitrioxide is heated above 400°, it decomposes into a mixture of iridium and its dioxide, and a little oxygen is at the same time evolved. The properties of the hemitrioxide depend on its mode of preparation ; it may form a colloidal soln. with hydrochloric acid ; and it may be insoluble in acids ; and in molten potassium hydrosulphate. J. J. Berzelius observed that the sesquioxide is reduced by hydrogen gas at ordinary temp., and the reduction is accompanied by a rise of temp. ; and that when heated in the presence of organic substances reduction proceeds with explosive violence. J. J. Berzelius thought that the various products obtained when iridium is oxidized by air or nitre in the presence of fused potassium hydroxide contain **potassium periridite,** and similarly with the precipitate obtained by adding potash lye to iridium trichloride. C. Claus showed that some of the colour effects obtained were due to J. J. Berzelius using iridium contaminated with some ruthenium. The products obtained by fusing potassium hydroxide with iridium under oxidizing conditions contain iridates (*q.v.*). L. N. Vauquelin observed that when milk of lime is added to an acid soln. of the blue oxide, a blue compound is precipitated ;

and C. Claus obtained a **calcium periridite,** $3CaO.Ir_2O_3$, or $Ca_3(IrO_3)_2$, as a dirty-yellow precipitate, on boiling an alkali chloroperiridite with an excess of lime water. The precipitate turns blue on exposure to air.

According to C. Claus, the *hydrate,* $Ir_2O_3.5H_2O$, or **iridium trihydroxide,** $Ir(OH)_3.H_2O$, is formed as an olive-green precipitate when the theoretical quantity of potassium hydroxide is added to a soln. of a chloroperiridite; no precipitation occurs if an excess of the precipitant be employed, since the hydrated oxide then dissolves as fast as it is formed, yielding an olive-green soln. from which the hydrate is precipitated by acids. The precipitated oxide readily oxidizes in air; it dissolves in acids to form a green soln.; the soln. in alkali lye readily oxidize when boiled in air, or when treated with hydrogen dioxide, and hydrated iridium dioxide is precipitated. C. Birnbaum observed that boiling alcohol reduces the hydrated hemitrioxide to iridium black. W. Palmaer obtained a soln. of **iridium hexamminotrihydroxide,** $[Ir(NH_3)_6](OH)_3$, by treating a soln. of the corresponding chloride with silver oxide. The soln. is strongly alkaline; it displaces ammonia from ammonium salts; it precipitates hydroxides from some metal salt soln.; and it absorbs carbon dioxide from the atmosphere to form a carbonate. The base, **iridium aquopentamminotrihydroxide,** $[Ir(NH_3)_5(H_2O)](OH)_3$, is produced by the action of silver oxide on the corresponding chloride. C. Claus prepared **iridium hydroxypentamminohydroxide,** $[Ir(NH_3)_5(OH)](OH)_2$. The hydroxypentammines were studied by B. E. Dixon.

According to C. Claus, **iridium dioxide,** IrO_2, is deposited in a hydrated form when a soln. of iridium chloride is boiled with alkali lye. The precipitate can be deprived of its water by heat. L. Wöhler and W. Witzmann recommended treating a hot soln. of sodium chloroiridate with alkali lye, and oxidizing the hemitrioxide by passing a current of oxygen through the liquid. The precipitated dioxide is dried at 400° in an atm. of carbon dioxide, and boiled first with alkali lye and then with sulphuric acid. The hydrate can be dehydrated at 760°. G. Geisenheimer obtained the anhydrous dioxide by melting potassium iridate with an excess of potassium bromide and chloride; extracting the cold product with water, treating the idsoluble residue with aqua regia to extract unchanged iridate, and drying the crystalline product at 100°. The dioxide is formed in an amorphous condition by heating to redness finely-divided iridium in a current of air or oxygen, for many hours, until a constant weight has been attained. W. Witzmann, and L. Wöhler and W. Witzmann said that the optimum temp. is 1070°.

G. Geisenheimer said that the black crystals are acicular. According to V. M. Goldschmidt, the crystals are tetragonal, and the X-radiograms correspond with the lattice parameters $a=4{\cdot}49$ A., $c=3{\cdot}14$ A., and $a:c=1:0{\cdot}699$. The sp. gr. is 3·15, and the mol. vol. 31·7. G. Lunde studied the subject. W. Witzmann, and L. Wöhler and W. Witzmann observed that when the dioxide is heated, it decomposes into oxygen and the metal. The dioxide and metal are to some extent mutually soluble, so that after a certain amount of dissociation has occurred, the solid phase contains two sat. solid soln., and yields a constant dissociation press. F. Becker gave for the dissociation press., p mm.:

	910°	937°	963°	982°	1004°	1029°
p . . .	37·0	56·5	86·9	119·1	164·5	237·5

L. Schmitt found that the sp. ht. of IrO_2 is 0·0587, and the mol. ht. 13·2. F. M. Jäger discussed the subject. L. Wöhler and N. Jochum gave for the mol. ht. $C=13{\cdot}329+0{\cdot}015216\theta$. L. Wöhler and W. Witzmann found that the oxidation proceeds most rapidly at 1070°, and at that temp. the heat of the reaction $Ir+O_2=IrO_2+50{\cdot}0$ Cals. L. Wöhler and N. Jochum gave 40·14 Cals. A. Götz gave 41·990 Cals. at 17°, and by Nernst's theorem, at 0°, 40·112 to 41·500 Cals. A. Götz gave $\log p=-Q/4{\cdot}571T+1{\cdot}75\log T+2{\cdot}8$, so that at 918° for $p=0{\cdot}723$ atm., $Q=50{,}760$ cals. and at 1093° for $p=0{\cdot}8921$ atm., $Q=52{,}055$ cals. L. Wöhler and N. Jochum gave for the heat of formation 40·14 Cals. C. Claus said that at the

temp. of calorescence—or glowing which occurs when the dioxide is heated in a current of carbon dioxide—all the water and a little oxygen is lost, and the oxide becomes insoluble in acids. F. Becker attributed the phenomenon to an abrupt change in the surface energy of the particles. Anhydrous iridium dioxide is insoluble in acids and alkalies, and it is easily reduced by hydrogen. S. Pastorello observed that the dioxide is stable in a current of sulphur dioxide up to 650°, but beyond that reduction occurs as shown by the appearance of iridium lines in the X-radiogram of iridium dioxide, Fig. 6. The decrease in the catalytic activity of platinum containing iridium is attributed to the formation of this oxide—*vide* rhodium sesquioxide. M. le Blanc and H. Sachse said that the electrical conductivity of the oxide is small; A. N. Guthrie and L. T. Bourland discussed the magnetic properties.

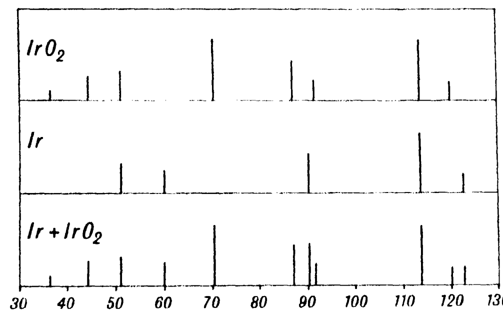

FIG. 6.—X-radiograms of Iridium and Iridium Dioxide.

J. J. Berzelius thought that the indigo-blue precipitate obtained when potassium chloroiridate or iridium tetrachloride is boiled with alkali carbonate is hydrated hemitrioxide, but C. Claus showed that the precipitate is the *dihydrate* of iridium dioxide, or **iridium tetrahydroxide,** $Ir(OH)_4$; any sesquioxide formed at the same time is converted to the dioxide by boiling in air, by adding hydrogen dioxide, or by passing a current of oxygen through the liquid. L. de Boisbaudran obtained the same hydrate by adding alkali to a soln. of a double sulphate of iridium in the presence of air; N. K. Pschenitsin and C. E. Krasikoff, by adding a 10 per cent. soln. of potassium hydroxide to a soln. of potassium chloroiridate, washing the product with water, and drying in vacuo; G. Geisenheimer, by boiling potassium iridate for several hours in a soln. of ammonium chloride, and also by similarly boiling the blue soln. obtained in the preparation of potassium iridate with ammonium chloride; as well as by heating to redness for 2 or 3 hrs. a mixture of finely-divided iridium and sodium hydroxide and nitrate, and extracting the soluble matters with water—here, the sodium iridate which is formed is decomposed by the water leaving the hydrated oxide as a residue. According to L. Wöhler and W. Witzmann, the precipitated hydrated oxide can be dried at 400° in a current of carbon dioxide, and then boiled with alkali lye, and subsequently treated with sulphuric acid.

The colour of the hydrated dioxide depends greatly on the proportion of water present. When dried in a desiccator over sulphuric acid, it contains approximately $2H_2O$, and is black; the water can only be driven off completely by heating at 760°. The anhydrous dioxide is also black. The freshly-precipitated dioxide is much more soluble in acids, and alkalies than when dried. C. Claus observed a momentary glowing—calorescence—when the hydrate is heated in an atm. of carbon dioxide—*vide supra*. The hydrate is almost insoluble in dil. sulphuric acid, and nitric acid; but it is slowly and completely "dissolved" by hydrochloric acid, forming a soln. which is at first indigo-blue, and afterwards becomes chrome-green, and finally reddish-brown when heated. According to L. Wöhler and W. Witzmann, the soln. of the amorphous, hydrated oxide in hydrochloric acid contain **colloidal iridium dioxide.** The violet colloidal soln. is obtained by the action of potassium hydroxide on sodium chloroiridate in the cold. The liquid gradually becomes violet, and, after a time, a blue modification separates. When the violet form is boiled, it becomes blue. The change in colour from indigo-blue to blue is attributed to the aggregation of colloidal particles.

A. Joly and E. Leidié heated potassium iridium nitrite in vacuo at 440°, and washed the product. There was formed a brown colloidal soln. of hydrated iridium dioxide, and a heavy black powder corresponding with **potassium hyperiridite,** $K_2O.6IrO_2$, and considered to be $(IrO)_6O_5(OK)_2$, or $6IrO(OH)_2$; if the double nitrite is heated to incipient redness in a muffle, and the product thoroughly washed with water, the residue has the composition $12IrO_2.K_2O$, considered to be $(IrO)_{12}O_{11}(OK)_2$. The individuality of these substances has not been established. H. St. C. Deville and H. Debray fused iridium with litharge and carbon, cupelled the button at a white-heat, and obtained a crystalline powder which was washed with acetic acid. It corresponds with **lead hyperiridite,** $PbO.IrO_2$. It is reduced by hydrogen, and the lead can be separated from the iridium by nitric acid. The compound is not attacked by conc. nitric acid. The lead is volatilized when it is heated in the oxyhydrogen flame.

J. J. Berzelius said that **iridium trioxide,** IrO_3, is known only in combination, and L. Wöhler and W. Witzmann were unable to prepare the pure oxide. C. Claus observed that when finely-divided iridium is heated with potassium nitrate for two hours, and the mass is extracted with water, an indigo-blue soln. of a basic potassium iridate is formed, and a dark blue crystalline powder of an acidic **potassium iridate,** $K_2O.2IrO_3$. This powder when washed is neutral to litmus, and tasteless; and it gives off chlorine when it is dissolved in hydrochloric acid. The proportion of contained alkali is variable. G. Geisenheimer obtained $2K_2O.IrO_3.H_2O$ under somewhat similar conditions. L. Wöhler and W. Witzmann observed that the methods of preparation by fusing finely-divided iridium with potassium nitrate and alkali and with sodium peroxide, as well as by the anodic oxidation of an alkaline solution of the dioxide, yield products containing considerably less than the theoretical proportion of oxygen. Oxygen is also absorbed when the dioxide, mixed with alkali, is heated in oxygen, but not in the amount required to form the trioxide. In the absence of alkali, the dioxide does not absorb oxygen, from which the conclusion is drawn that a trioxide free from alkali is unstable, and that the comparative stability in the presence of alkali depends on the adsorption of the trioxide by the alkali.

F. Krauss and H. Gerlach prepared **iridium tetroxide,** IrO_4, by heating the hydroxide for a short time in nitrogen at 350°. The method employed by F. Krauss and H. Kukenthal for ruthenium trihydroxide (*q.v.*) furnishes **iridium tetrahydroxide,** $Ir(OH)_4$, free from chlorine and alkalies.

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§ 8. The Iridium Fluorides

According to H. Moissan,[1] iridium is not attacked by fluorine in the cold ; but at a dull red-heat a reaction occurs, and at a higher temp. a volatile fluoride is formed which appears as a white vapour. O. Ruff also noted that fluorine reacts only at a dull red-heat. E. Urichoechea dissolved the hydrated oxide in hydrofluoric acid, and on evaporating the green soln. to dryness, obtained a green mass of an **iridium fluoride** which was insoluble in water, and soluble in acids. When heated it became white, and then formed a brown powder.

O. Ruff and J. Fischer found that when finely-divided iridium is heated at 360° to 400° in a current of fluorine, **iridium hexafluoride,** IrF_6, and **iridium pentafluoride,** IrF_5, are formed. The yield of the pentafluoride is increased by raising the temp.

Iridium hexafluoride is a yellow solid with a tinge of green ; it melts at about 30°, and its vap. press. is then relatively high, about 320 mm., and at about 50°, the product boils at 760 mm. press. J. A. M. van Liempt studied the critical constants. O. Ruff and J. Fischer found that the salt is decomposed by the moisture of the atmosphere and gives off white fumes—producing hydrogen fluoride, ozone, and the pentafluoride. At room temp., it attacks the alkali of glass containing vessels, forming the pentafluoride and oxygen ; and light accelerates the reaction. The hexafluoride is more stable in vessels of fused quartz. When heated to 400° in air, it passes into the pentafluoride with sparking, and the simultaneous formation of the violet oxide, and oxygen.

Iridium pentafluoride is a white or greyish-white solid which is much less volatile than the hexafluoride. When kept in glass vessels, it becomes greyish-black and violet, and forms oxides, and oxyfluorides ; this reaction is very rapid at 100° to 200°.

H. I. Schlesinger and M. W. Tapley prepared **potassium fluoiridate,** K_2IrF_6, by the action of finely-divided iridium on $3KF.HF.PbF_4$. They also prepared **lead fluoiridate,** $PbIrF_6$; and studied the absorption spectra.

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§ 9. The Iridium Chlorides

S. Streicher,[1] and L. Wöhler and S. Streicher prepared **iridium monochloride,** $IrCl$, by the thermal decomposition of iridium dichloride, in an atm. of chlorine at about 790°. Its range of stability is 773° to 798° in an atm. of chlorine. The monochloride furnishes copper-red crystals of sp. gr. 10·18, and it is insoluble in alkalies, and acids—even conc. sulphuric acid. The molecular heat of formation is 20·55 Cals. The vap. press., p mm., are :

	698°	739°	749°	751°	771°	773°	799°
p .	153	256	290	322	424	455	771 mm.

J. J. Berzelius described the preparation of **iridium dichloride,** or **iridous chloride,** $IrCl_2$, in a number of ways—*e.g.*, by exposing finely-divided iridium at an incipient red-heat to chlorine gas; and by the action of hydrochloric acid on hydrated iridium monoxide—and C. Claus considered them all to be either the trichloride, or mixtures of the trichloride and the metal. The grey product obtained by the action of chlorine on iridium was said to be a mixture of the trichloride and metal, for, when finely-powdered and again exposed to the action of chlorine, it absorbs that gas without change of colour, and thus approaches more nearly to the state of the trichloride; and when mixed with sodium chloride and treated with chlorine as before, and the cold product leached with water, some iridium remains. Again, if the tetrachloride be reduced by stannous chloride, sulphur dioxide, hydrogen sulphide, potassium ferrocyanide, or alcohol, the reduction stops at the trichloride stage except in cases where the metal is separated without the intermediate formation of the dichloride. L. R. von Fellenberg said that the dichloride is produced when iridium disulphide is heated in chlorine gas; M. Skoblikoff observed that the thermal decomposition of the tetrachloride yields the dichloride like a brown resin which W. Palmaer said is of an uncertain composition; and K. Seubert described some complex alkali sulphites associated with iridium dichloride. All this shows that the dichloride has not been isolated, or else it shows that the dichloride has a very narrow range of stability. L. Pauling discussed the lattice structure. The observations of S. Streicher, and L. Wöhler and S. Streicher, show that the dichloride is stable only in the range of temp. 763° to 773° in chlorine gas; above 773°, it dissociates into the monochloride and chlorine. It is produced when the trichloride is ignited at 770° in an atm. of chlorine. The brown crystals of the dichloride so formed are insoluble in alkalies, and acids—even conc. sulphuric acid. The observations of V. M. Goldschmidt, and G. Bruni and A. Ferrari, indicate that the crystals are probably rhombohedral. S. Streicher, and L. Wöhler and S. Streicher found the mol. heat of formation from its elements is 20·05 Cals. The vap. press., p mm., are:

	711°	737°	749°	755°	771°
p	241	386	505	548	731 mm.

J. J. Berzelius noted the formation of a light greenish-grey powder when potassium or ammonium chloroiridite is treated with aq. ammonia, and his rough analysis indicates that an ammine was formed. M. Skoblikoff, and W. Palmaer obtained **iridous dichlorodiammine,** $[Ir(NH_3)_2Cl_2]$, by warming a mixture of iridium dichloride with an excess of ammonium carbonate, and then neutralizing the liquid with hydrochloric acid. The yellow, granular powder is insoluble in water; and if it be boiled with an excess of ammonia, yellowish-white **iridous tetramminochloride,** $[Ir(NH_3)_4]Cl_2$, separates as the soln. cools. It gives off ammonia when boiled with water. K. Seubert prepared **ammonium sulphitochloroiridite,** $IrCl_2.H_2SO_3.4NH_4Cl$, and $IrCl_2.(NH_4)_2SO_3.2NH_4Cl$; **ammonium potassium sulphitochloroiridite,** $IrCl_2.K_2SO_3.2NH_4Cl.4H_2O$. W. Manchot and H. Gall prepared **iridous dicarbonyldichloride,** $Ir(CO)_2Cl_2$.

J. J. Berzelius reported **iridium trichloride,** $IrCl_3$, to be formed as a sublimate when iridium alone, or admixed with potassium nitrate, is heated in chlorine; or when "iridium dichloride" is heated. As indicated above, C. Claus showed that J. J. Berzelius' dichloride is either the trichloride or a mixture of the trichloride with metal; and added that the trichloride is the most stable of all the iridium chlorides. C. Claus, and L. Wöhler and S. Streicher prepared the trichloride by heating the reduced metal, mixed with sodium chloride, in a current of chlorine, at 600° to 620°. The reaction is completed in a few minutes. F. Krauss and H. Gerlach observed that the formation of the trichloride from iridium and chlorine is accelerated by light, and by the presence of carbon monoxide. Iridium tetrahydroxide reacts with chlorine, when heated, forming the trichloride. E. Leidié obtained the trichloride by heating ammonium chloroiridate, or iridium tetra-

chloride, in a current of chlorine at 440°, and cooling the product in carbon dioxide.

J. J. Berzelius obtained an impure trichloride by heating iridium mixed with potassium nitrate, extracting the cold mass with hot nitric acid, dissolving the washed product in hydrochloric acid, and evaporating the soln. to dryness. A similar product was obtained by heating the yellow powder produced by the action of sulphuric acid on an alkali chloriridite in hydrogen chloride at 500°. According to M. Delépine, the products obtained by heating hydrated hydrochloriridic acid, $H_2IrCl_6.6H_2O$, are associated with traces of hydrogen chloride and water, and they are soluble in water; the ordinary anhydrous salt is insoluble. If the aq. soln. be concentrated, and the crystals dried at 100°, there remains the *hemitrihydrate*, $IrCl_3.1\frac{1}{2}H_2O$. The *tetrahydrate*, $IrCl_3.4H_2O$, described by C. Claus, by evaporating an acidic soln. of the trichloride, is an indefinite mixture of iridium trichloride with hydrogen chloride and water.

L. Wöhler and S. Streicher, and S. Streicher found that strongly sintered iridium powder which has been heated to 900°, forms a brown trichloride at 600°; if this product is reduced in hydrogen at low temp. and again chlorinated at 600°, the yellow trichloride is obtained. On further reduction and chlorination the dark green trichloride results. During these alternating processes the metal produced at the various stages becomes more and more finely divided, that is, more and more rich in surface energy; the same holds for the oxide obtained from the metal. The various trichlorides therefore owe their colours to the varying stages of fineness of the particles, that is, they are simply surface modifications as shown by measurements of their absorptive power towards methylene-blue, and of their velocity of sedimentation. The dissociation press. of these different specimens of trichlorides show large differences in accord with the difference in their surface energies. The dissociation press., p mm., for a brownish-green sample are:

	442°	447°	521°	591°	650°	671°	708°	748°
p . . .	21	24	43·5	84	163	221	486	570 mm.

for a sample prepared at 730°:

	643°	682°	716°	749°	756°
p	88	165	301	555	627 mm.

and for samples:

	Brownish-black			Yellow		Dark olive-green	
	618°	685°	764°	650°	751°	674°	767°
p . . .	119	367	767	178	577	499	807 mm.

L. Wöhler and F. Müller's observations for the range of stability of the chlorides are summarized in Fig. 7.

Iridium trichloride furnishes olive-green, yellow, or dark brown crystals of sp. gr. 5·30. The limits of stability of the salt range from below 100° upwards to 763°. It is appreciably volatile at 470°. A. N. Guthrie and L. T. Bourland found that the diamagnetic susceptibility is independent of temp. D. M. Bose and H. G. Bhar, and L. A. Welo and K. Baudisch studied the magnetic properties. The trichloride dissociates above 763° into iridium dichloride and chlorine. Its mol. heat of formation is 19·87 Cals.

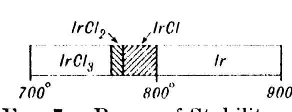

Fig. 7.—Range of Stability of the Iridium Chlorides.

V. Ipatéeff and J. Andreevsky studied the precipitation of metal by hydrogen under press. The anhydrous salt is insoluble in water, alkalies, and acids—it even resists attack by conc. sulphuric acid, and aqua regia. The green crystals of the hydrate are soluble in water, forming a greenish-yellow soln. A. B. Lamb and L. T. Fairhall found that the rate of conversion of the aquo-salt, at 95°, is in accord with a unimolecular reaction; and that with soln. having 0·00093, 0·0038, and 0·0157 mol. per litre, the percentages of aquo-salt formed are respectively 26·1, 4·5,

and 6·0. According to H. Rose, the aq. soln. is oxidized by chlorine to the higher chloride. C. Claus found that unlike the corresponding platinum or palladium salt, the soln. of iridium trichloride does not change potassium iodide. H. Rose observed that hydrogen sulphide slowly colours the soln. brown without the separation of sulphur, and with hot soln., iridium sulphide is formed, coloured, according to A. Bettendorff, a pale orange-yellow; H. Rose found that ammonium sulphide gives a brown precipitate. M. C. Lea said that tetrathionic acid gives a wine-red coloration in acidic soln., and it is not changed if the soln. be made ammoniacal.

H. Rose observed that ammonia does not change the cold soln., but when boiled, the liquid becomes at first black, and after standing some time, dark violet-blue. O. W. Gibbs found that potassium nitrite produces no perceptible change in cold soln., but, when boiled or allowed to stand for some time, the green liquid becomes yellow owing to the formation of a soluble double salt which is precipitated by alcohol. H. Rose observed that the soln. is oxidized to a higher chloride by nitric acid, or by aqua regia, but J. Fiedler observed that iridium chloride, in the presence of oxalic acid, is reduced when the soln. is exposed to light. G. Geisenheimer prepared some **iridium phosphochloride,** $IrCl_3.2PCl_3$, insoluble in water; $IrCl_3.3PCl_3$, also obtained by W. Strecker and M. F. Schurigin, and M. F. Schurigin—G. Geisenheimer prepared the monohydrate; IrP_3Cl_{15}, or $IrCl_4.PCl_5.2PCl_3$, decomposed by water into iridium trichloride, and phosphorous and phosphoric acids, **iridium phosphoarsenochlorides,** $2IrP_3Cl_{15}.5AsCl_3$, decomposed by water; and $IrCl_3.2PCl_3.2AsCl_3$, was also decomposed by water; and **iridium phosphosulphochloride,** $IrCl_3.2PCl_3.2SCl_2$. W. Manchot and H. Gall observed that at 150°, carbon monoxide converts iridium trichloride into **iridium dicarbonyldichloride,** $Ir(CO)_2Cl_2$, which melts at 140°, is unstable particularly towards moisture, which hydrolyzes it into iridium oxide or hydrated oxide, hydrochloric acid, and carbon monoxide.

No change was observed with potassium ferricyanide, and with potassium ferrocyanide, a slight turbidity appears after some time. M. C. Lea observed that a soln. of potassium ferricyanide in soda lye, colours an ammoniacal soln. of iridium trichloride yellow, and when boiled, a deep wine-red colour. H. Rose observed no change is produced by sodium formate in cold soln., but with hot soln., iridium is precipitated; no precipitate is produced by oxalic acid. C. Claus found that no precipitate is produced when potassium hydroxide is added to a soln. of iridium trichloride, but on heating the yellow liquid, an indigo-blue coloration is developed, and dark blue hydrated dioxide is deposited as oxygen is absorbed from the air. H. Rose reported that soln. of alkali carbonates produce no change in cold soln., but when boiled the colour changes to black and, on standing for a long time, blue; barium carbonate does not precipitate the hydrated oxide in hot or cold soln.; soln. of sodium phosphate have no perceptible effect; borax in hot soln. gives a greyish-blue opalescence; mercurous nitrate gives a yellow precipitate; and silver nitrate gives a brownish-white precipitate, which, according to M. Delépine, when dried at 110° is **silver hydroxychloroperiridite,** $IrCl_3.AgOH$. S. Royama found that copper precipitates 1 to 3 per cent. of the iridium in an acidic soln. of the chloride. O. W. Gibbs found that cobaltic hexamminochloride gives a pale yellow precipitate of the corresponding **cobaltic hexamminochloroperiridite.**

F. Krauss and H. Gerlach observed that iridium tetrahydroxide reacts with hydrogen chloride at ordinary temp., forming **iridium aquohydroxydichloride,** $[Ir(H_2O)(OH)Cl_2].2H_2O$; and when the *dihydrate* is heated it forms the anhydrous salt which when dissolved in water, forms **dichlorodihydroxyiridic acid,** $H[Ir(OH)_2Cl_2]$. When the aquohydroxydichloride is treated with hydrogen chloride, it yields **iridium aquotrichloride,** $[Ir(H_2O)Cl_3]$, which loses its water at 310°, forming the trichloride. M. Delépine and P. Boussi studied the dehydration of these chlorides, but obtained no evidence of the polymerization of the contained water.

J. J. Berzelius observed that aq. ammonia produces a greyish-white precipitate when it acts on potassium chloroiridate, and the analysis indicates that an ammine

was probably formed. W. Palmaer prepared **iridium hexamminochloride,** $[Ir(NH_3)_6]Cl_3$, by heating the corresponding chloropentamminochloride with 25 per cent. aq. ammonia in a sealed tube at 140°. The product is purified by conversion to nitrate, repeated evaporation with conc. hydrochloric acid, and crystallization from ice-cold hydrochloric acid soln. The six-sided, colourless crystals are monoclinic, with the axial ratios $a:b:c=0\cdot5843:1:0\cdot6502$, and $\beta=57°\ 31'$; the sp. gr. is 2·4335 at 15·5°; and the mol. vol. is 165·1. Similar cobalt, chromic, and rhodium salts, soluble in water, are known—G. Beck studied the ionization of the salt. W. Palmaer observed that 1 part of the salt dissolves in 4·5 to 5·0 parts of water at room temp. Soln. of the hexammines with hydrochloric acid give an incomplete precipitation; 30 per cent. nitric acid precipitates the nitrate; hydrobromic acid precipitates the bromide, and potassium bromide gives an incomplete precipitation; potassium iodide precipitates the iodide, and similarly with hydriodic acid; hydrofluosilicic acid gives a precipitate; ammonium sulphate, no precipitate; ammonium oxalate, a precipitate; neutral potassium chromate, a pale yellow precipitate; potassium dichromate, an orange-red precipitate; barium dithionate, a precipitate; sodium phosphate, no precipitate, but with ammonia as well, a precipitate; sodium pyrophosphate, a precipitate; mercuric chloride, a white precipitate; mercuric cyanide, no precipitate; potassium ferricyanide, a precipitate; potassium ferrocyanide, a white precipitate; gold chloride, a yellow precipitate; iridium trichloride, a double salt; iridium tetrachloride, a brown precipitate; platinic chloride, a brownish-yellow precipitate; and platinic chloride and sulphuric acid, a yellowish-brown precipitate. When the soln. of the hexamminochloride is treated with potassium chloroperiridite, **iridium hexamminochloroperiridite,** $[Ir(NH_3)_6]IrCl_6$, is deposited as a yellow powder which can be crystallized from aq. soln. An isomorphous rhodium salt is known. Sulphuric acid attacks the salt only above 190°. W. Palmaer observed that if the chloropentamminochloride is treated with conc. potash lye for several hours, and the cold, filtered liquid mixed with conc. hydrochloric acid, **iridium aquopentamminochloride,** $[Ir(NH_3)_5H_2O)]Cl_3$, is precipitated; it is washed with cold, conc. hydrochloric acid, and alcohol. The aq. soln. is again precipitated by cold conc. hydrochloric acid for crystallization. The sp. gr. is 2·473 at 15°/4°; and the mol. vol., 162·8. Similar chromic and cobaltic salts are known. The mol. conductivity of soln. of a mol of salt in 250, 500, and 1000 litres of water at 25° are, respectively, 362·1, 382·8, and 399·5. The salt loses water at 100°, forming the chloropentamminochloride. It is soluble in water—1 part of the salt dissolves in 1·2 to 1·5 parts of water at room temp. When chlorine water is added to the aq. soln., the violet soln. becomes successively dark blue, pale blue, and green; the green soln. turns brown when ammonia is added. Hydrochloric acid precipitates the aquopentamminochloride; nitric acid precipitates the nitrate; potassium iodide soln., no precipitate, but solid potassium iodide precipitates the iodide; hydrofluosilicic acid gives no precipitate, but if alcohol is added, a white precipitate; ammonium oxalate, a white precipitate, potassium dichromate, a black precipitate, barium dithionate, no precipitate; sodium phosphate, no precipitate; sodium pyrophosphate, a white precipitate; mercuric cyanide, a white precipitate in a short time; potassium ferricyanide, a reddish, brown precipitate; potassium ferrocyanide, a white precipitate; gold chloride, an orange-yellow precipitate; iridium trichloride, a precipitate of the complex salt; iridium tetrachloride, a dirty-grey precipitate; and potassium chloroiridate, a brownish-yellow precipitate. The soln. of the aquopentamminochloride gives a yellow precipitate with chloroplatinic acid, **iridium aquopentamminochloroplatinate,** $[Ir(NH_3)_5H_2O]_2(PtCl_6)_3$, and similarly with platinic chloride and dil. sulphuric acid.

C. Claus, W. Palmaer, and A. B. Lamb and L. T. Fairhall prepared **iridium chloropentamminochloride,** $[Ir(NH_3)_5Cl]Cl_2$, in wine-red crystals, by the action of ammonia on iridium trichloride or tetrachloride, or the chloro-double salts; and it is also obtained in yellow crystals, by the action of barium chloride on the

corresponding sulphate. The red colour of the first product is due to the presence of a little iridium trichloride, which can be removed by the action of hydrogen sulphide on the hot soln., and filtering. The yellowish-white, octahedral crystals are isomorphous with the corresponding chromic, cobaltic, and rhodium salts. The rhombic crystals have the axial ratios $a:b:c=0\cdot98727:1:1\cdot5527$; the sp. gr. is 2·679 at 15·5°; and the mol. vol., 143·6. W. Biltz gave 2·672 for the sp. gr. The mol. conductivities of a soln. of a mol of the salt in 125, 250, and 500 litres of water at 25° are, respectively, 230·9, 243·2, and 250·3, or, by extrapolation for $\nu=1000$, $\epsilon=255\cdot5$. The salt is not altered by heating it to 275°, but above this temp. it decomposes into iridium, etc. The salt is soluble in water—150·6 parts of water at 13·8° are required for the dissolution of 1 part of the salt; and 10,000 c.c. of 10 per cent. hydrochloric acid dissolve 1 part of the salt. A. B. Lamb and L. T. Fairhall measured the rate of hydrolysis with the aquopentammine—*vide supra*. The chlorine atom in the complex is not removed by silver nitrate, or sulphuric acid. When treated with iridium trichloride, yellow **iridium chloropentamminochloroperiridite,** $[Ir(NH_3)_5Cl]_3(IrCl_6)_2$, is formed. A similar rhodium salt is known. W. Palmaer made **iridium chloropentamminochloroplatinate,** $[Ir(NH_3)_5Cl]PtCl_6$. The chloropentamminochloride is decomposed slightly at 200°, and at a red-heat it decomposes into iridium, etc.; and it is slowly attacked by sulphuric acid at 110°. M. Guillot obtained **iridium trichlorotrispicoline,** $[Ir(\alpha-C_5H_4(CH_3)N)_3Cl_3]$; M. Delépine, **iridium diaquodichlorobispyridine,** $[Irpy_2(H_2O)_2Cl_2]$, as a salt of tetrachlorobispyridine. He also obtained **iridium trichloro-1, 2, 6-trispyridine,** $[Irpy_3Cl_3]$, and **iridium trichloro-1, 2, 3-trispyridine.** When a soln. of the chloropentamminochloride is treated with silver oxide, or the soln. is warmed with sodium hydroxide on a water-bath, a soln. of **iridium chloropentamminohydroxide,** $[Ir(NH_3)_5Cl](OH)_2$, is formed. The soln. absorbs carbon dioxide from the air, and is slowly decomposed when boiled. This salt was also prepared as a monohydrate by B. E. Dixon, who also obtained **iridium hydroxypentamminochloride,** $[Ir(NH_3)_5(OH)]Cl_2.H_2O$. P. C. Ray and N. Adhikari obtained complexes with **ethylamine,** and **ethyl sulphide.**

A. Werner and O. de Vries, and W. Palmaer found that when the dinitritotetramminochloride is heated with ammonium chloride and conc. hydrochloric acid for several hours, the yellow liquid evaporated for crystallization, filtered, and the aq. extract treated with hydrochloric acid, yellow needles and prisms of **iridium dichlorotetramminochloride,** $[Ir(NH_3)_4Cl_2]Cl.H_2O$, separate out. The salt can be purified by crystallization from the hot, acidulated soln. The pale yellow monoclinic crystals have the axial ratios $a:b:c=0\cdot72078:1:0\cdot65354$, and $\beta=53°\ 13'$. H. Bäckström said that the crystals are trigonal with the axial ratios $a:c=1:0\cdot64497$. The refractive indices for Na-light are $\epsilon=1\cdot6666$, and $\omega=1\cdot6576$, and the double refraction is positive, and $\epsilon-\omega=0\cdot00904$. The salt loses water when heated, and at a higher temp. decomposes into iridium, etc. W. Biltz gave 2·679 for the sp. gr. The mol. conductivities of soln. with a mol. of the salt in 125, 250, and 500 litres of water at 25° are, respectively, 95·05, 100·05, and 103·00, or, by extrapolation, for $v=1000$, $\mu=104\cdot5$. E. Rosenbohm studied the magnetic susceptibility. Chlorine water colours the aq. soln. violet. One part of the salt dissolves in 15 parts of water at room temp. The salt is not attacked by conc. hydrochloric acid. A soln. of tetrammine with nitric acid gives a small precipitate; with conc. hydrobromic acid, a precipitate; with conc. hydriodic acid, a pale yellow precipitate; with hydrofluosilicic acid, no precipitate; with ammonium oxalate, no precipitate; with neutral potassium chromate, a pale yellow precipitate; with potassium dichromate, a brick-red precipitate; with barium dithionate, a white precipitate; sodium phosphate, no precipitate either with or without the addition of ammonia; sodium pyrophosphate, no precipitate; mercuric chloride, a yellowish-white precipitate; potassium ferrocyanide or ferricyanide, no precipitate; gold chloride, an orange-red precipitate; iridium trichloride, a double salt; iridium tetrachloride, a brown precipitate; platinic

chloride, a yellow precipitate, and along with sulphuric acid, an orange precipitate. When the aq. soln. is treated with iridium trichloride, or potassium chloroperiridite, a pale yellow precipitate of **iridium dichlorotetramminochloroperiridite,** $[Ir(NH_3)_4Cl_2]_3(IrCl_6)$, is formed. The salt is soluble in water; and the hot, conc. soln. on cooling deposits the salt in yellow needles. L. A. Tschugaeff obtained **pentachlorohydrazinoiridic acid,** $H[Ir(N_2H_5)Cl_5]$, by the action of hydrazine hydrate on potassium chloroiridate; with tetramminoplatinous chloride it yields **platinum-tetrammine pentachlorohydrazinoiridate,** $[Pt(NH_3)_4][Ir(N_2H_5)Cl_5]_2$; and with cæsium chloride, **cæsium pentachlorohydrazinoiridate,** $Cs[Ir(N_2H_5)Cl_5]$. E. Ogawa observed that when pyridine is progressively added to **aquopentachloroperiridous acid,** the aquo-group is first displaced and pentachloropyridinoperiridous acid, $H_2[IrpyCl_5]$, is first formed; then **pyridinium pentachloropyridinoperiridite,** $(C_5H_6N)_2[IrpyCl_5]$; then **pyridinium tetrachlorobispyridinoperiridite,** $(C_5H_6N)[Irpy_2Cl_5]$; and finally, **iridium trichlorotrispyridine,** $[Irpy_3Cl_3]$; this product is also obtained by adding pyridine to the chloroiridate. M. Guillot prepared **iridium trichlorotrispicoline,** $[Ir(C_6H_7N)_3Cl_3]$; **iridium tetrachlorbispicoline,** $[Ir(C_6H_7N)_2Cl_4]$; and **iridium trichlorodiaquopicoline,** $[Ir(C_6H_7N)(H_2O)_2Cl_3]$. P. C. Ray and co-workers studied some complexes with methyl sulphide.

A. Werner and O. de Vries observed that **iridium trichlorotriammine,** $[Ir(NH_3)_3Cl_3]$, is probably formed when the trinitritotriammine is heated with ammonium chloride, and hydrochloric acid at 180° for 9 hrs. The yellow product was impure. W. Palmaer obtained the salt in quadratic, orange plates which are sparingly soluble in water, decomposed when strongly heated, and it is not acted on by hot sulphuric acid. According to M. Delépine, **iridium trichlorotrispyridine,** $[Irpy_3Cl_3]$, can be prepared from one of the forms—orange-yellow, or red—of potassium tetrachlorobispyridine at 130°. The orange-yellow form furnishes two isomerides, whilst the red modification yields only one compound. The orange-coloured salts and their products correspond throughout with the *cis*-form, and may give optical isomerides, whilst the red salts correspond with optically inactive *trans*-forms. V. V. Lebedinsky and co-workers prepared **iridium trichlorotriammino-salt** of the types $[IrR_3Cl_3]$; **iridium dichlorotetramminochloride,** $[IrR_4Cl_2]Cl$; **iridium chloropentamminochloride,** $[IrR_5Cl]Cl_2$; and **iridium hexamminotrichloride,** $[IrR_6]Cl_3$.

M. Delépine also prepared **iridium tetrachlorobispyridine,** $[Irpy_2Cl_4]$; **iridium dichlorobispyridinodiamminochloride,** $[Ir(NH_3)_2py_2Cl_2]Cl.H_2O$; **iridium chlorobispyridinotriamminochloride,** $[Ir(NH_3)_3py_2Cl]Cl_2.4H_2O$; and **iridium trispyridinotetramminochloride,** $[Ir(NH_3)_4py_2]Cl_3$. M. Delépine, and M. Delépine and J. Pineau observed that when iridium tetrachlorodipyridine, $[Irpy_2Cl_4]$, is treated with ammonia, it furnishes a mixture containing **iridium dichlorobispyridinodiammino-salt,** $[Irpy_2(NH_3)_2Cl_2][Irpy_2Cl_4]$, **iridium chlorobispyridinotriammino-salt,** $[Irpy_2(NH_3)_3Cl][Irpy_2Cl_4]_2$,—which also yields other halides, and the sulphate—and iridium tetrachlorobispyridine. They also prepared **iridium chloropyridinotetramminochloride,** $[Ir(NH_3)_4pyCl]Cl_2.2H_2O$, and they obtained the chloromercurate, the picrate, dichromate, and sulphate, as well as the complexes of $[Ir(NH_3)_4pyCl]$ with $[Irpy_2Cl_4]'$ and $[Irpy.Cl_5]''$. They also prepared **iridium aquobispyridinotriamminochloride,** $[Ir(NH_3)_3py_2(H_2O)]Cl_3.3H_2O$. When potassium dioxalatobispyridinoperiridite is treated with hydrogen chloride at 130°, it forms yellow needles of an oxalato-salt, and orange-yellow prisms of an **iridium dichloro-diaquobispyridine-salt** of iridium tetrachlorobispyridine, $[Irpy_2(H_2O)_2Cl_2][Irpy_2Cl_4]$, which, with ammonia, forms ammonium tetrachlorobispyridinoperiridite, and yellow crystals of **iridium hydroxyaquodichlorobispyridine,** $[Irpy_2(H_2O)(OH)Cl_2]$. F. Korten, and E. Rimbach and F. Korten prepared a complex **ammonium bispyridinium chloroperiridite,** $(NH_4)_3IrCl_6.2C_5H_6NCl$; and also **anilinium chloroperiridite,** $(C_6H_5NH_3)_3IrCl_6$.

J. J. Berzelius obtained **potassium chloroperiridite,** $K_3IrCl_6.3H_2O$, or $K_3[IrCl_6].3H_2O$, by the evaporation of a soln. of potassium chloride, and iridium trichloride, but C. Claus said that the salt examined by J. J. Berzelius must have contained a relatively large proportion of ruthenium. C. Claus obtained the salt by the action of sulphur dioxide or hydrogen sulphide on a soln. of potassium chloroiridate; and by heating to redness the chloroiridate alone, or with one-

third part of potassium carbonate, and washing the product with water. E. Leidié recommended nitric oxide as reducing agent in place of hydrogen sulphide in a vessel deprived of air by the passage of carbon dioxide. The compound is also formed when potassium chloroiridate is heated to 440° in a current of hydrogen chloride. H. Dufet said that the olive-green prisms of the *trihydrate* are tetragonal. C. Claus observed that the crystals effloresce in air and are freely soluble in water and insoluble in alcohol. A. Duffour obtained the *monohydrate*, $K_3IrCl_6.H_2O$, by the action of boiling hydrochloric acid on potassium oxalatoiridate. The brown, rhombic crystals are isomorphous with the corresponding rhodium salt. C. Claus observed that the air-dried salt loses its water of crystallization at 18°. The aq. soln. is olive-green by reflected light, purple-red by transmitted light. When the aq. soln. is boiled it deposits a green powder of **iridium oxychloride**; chlorine water, or aqua regia convert it into the chloroiridate; and an excess of alkali lye forms an olive-green soln. by the dissolution of the hydrated hemitrioxide—*vide supra*, iridium chloride. A. Duffour found that the monoclinic crystals of the pyridine complex, $KIrpy_2Cl_4.H_2O$, have the axial ratios: $a:b:c=1\cdot169:1:1\cdot439$, and $\beta=97°\ 54'$. C. Claus prepared some **potassium sulphitochloroperiridites,** $K_4Ir_2Cl_2(SO_3)_4.4KCl.12H_2O$, insoluble in cold water and decomposed by hot water; $K_4Ir_2Cl_2(SO_3)_4.2K_2SO_3$, decomposed by water; and $8KCl.Cl_2Ir_2(SO_3)_2.4H_2O$, insoluble in water, and alcohol.

M. Delépine prepared **rubidium chloroperiridite,** $Rb_3IrCl_6.H_2O$, in olive-green, needle-like crystals, by reducing the chloroiridate with an oxalate, and adding an excess of rubidium chloride to the soln. He obtained in a similar manner **cæsium chloroperiridite,** $Cs_3IrCl_6.H_2O$, in bright olive-green needles. J. J. Berzelius, and C. Claus prepared impure **ammonium chloroperiridite,** $(NH_4)_3IrCl_6.1\frac{1}{2}H_2O$, from a soln. of the component salts; and C. Claus, and M. Delépine, by reducing a soln. of ammonium chloroiridate as in the case of the potassium salt, or by the double decomposition of the sodium salt and an excess of ammonium chloride. A. Duffour, and A. Joly showed that the salt is probably a *monohydrate*, and isomorphous with the corresponding potassium salt, and with those of rhodium. According to W. Keferstein, the dark olive-green crystals are rhombic. When heated the salt begins to decompose just over 200°, and the ignition furnishes spongy iridium. C. Claus, and M. C. Lea observed that the salt is freely soluble in water. A. Benrath studied the photochemical reduction of the salt by oxalic acid. A. Duffour found that the monoclinic crystals of the pyridine complex, $NH_4Irpy_2Cl_4.H_2O$, have the axial ratios: $a:b:c=1\cdot192:1:0\cdot644$, and $\beta=94°\ 33'$.

C. Claus prepared **sodium chloroperiridite,** $Na_3IrCl_6.12H_2O$, by reducing a soln. of the chloroiridate with hydrogen sulphide; M. Delépine, by reducing the soln. with sodium oxalate; and E. Leidié, by heating the chloroiridate in hydrogen chloride at 440°. Dark green crystals separate from the aq. soln. V. V. Lebedinsky and co-workers also prepared this salt. J. C. G. de Marignac said that the crystals are rhombohedral; and C. Karmrodt and E. Uhrlaub, that they are monoclinic. The crystals melt in their water of crystallization at 50°. E. Ogawa found that the vap. press., p mm., of a sat. aq. soln. of the *dodecahydrate* is:

	15°	18°	25°	32°	36°	41°	47°	54°	63·2°	68°
p .	10·46	12·62	19·58	28·55	34·38	42·34	54·99	77·42	119·53	149·29

or, below 28·7°, $\log p=9\cdot10835-2329\cdot41T^{-1}$; between 28·7° and 48·0°, $\log p=7\cdot50169-1843\cdot94T^{-1}$; and above 48·0°, $\log p=8\cdot79301-2256\cdot94T^{-1}$. There are points of inflexion at 28·7° and 48·0°. The water solubility, S grms. anhydrous salt in 100 grms. of water, is, at

	15°	25°	35°	40°	45°	51°	60°	70°	80°	85°
S .	3·146	46·11	74·03	96·00	123·96	155·26	191·18	231·66	279·34	307·26

There are points of inflexion on the curve at 29° and 48·6°. When the dodecahydrate is kept over sulphuric acid in vacuo for an hour at 15° to 43°, the *dihydrate* is formed.

There is a sudden change in the heat of soln. at 28·9°, but no change in composition occurs above or below 28·9°. Hence, the *a-dodecahydrate* is stable below 28·9°, and the *β-dodecahydrate* is stable above that temp. The β-dodecahydrate changes to *β-dihydrate* at 48·3°. The *a-dihydrate* is obtained by keeping the a-dodecahydrate in vacuo over sulphuric acid, and it has the same colour as the β-dihydrate. The β-dihydrate does not lose water at 100°. E. Ogawa also studied the oxidation-reduction potential in the system Na_3IrCl_6–Na_2IrCl_6.

According to M. Delépine, when a soln. of lithium chloroiridate is boiled with a little alcohol, and evaporated, it forms **lithium chloroperiridite,** $Li_3IrCl_6.12H_2O$. The salt is best obtained by reducing the chloroiridate with lithium oxalate in aq. soln. The black, deliquescent rhombohedra are freely soluble in water, and in alcohol. A mixed soln. of sodium and lithium chloroperiridates first deposits on evaporation the sodium salt alone; but on concentrating the liquid further, hexagonal prisms of **disodium lithium chloroperiridite,** $Na_2LiIrCl_6.12H_2O$, are formed, and later, hexagonal needles of **sodium dilithium chloroperiridite,** $NaLi_2IrCl_6.12H_2O$. These salts are stable in soln. only in the presence of an excess of a salt richer in lithium.

C. Claus prepared **silver chloroperiridite,** Ag_3IrCl_6, by adding an excess of silver nitrate to a soln. of sodium chloroiridate, and allowing the blue, flocculent precipitate of silver chloroiridate to stand for some time when it becomes colourless or yellow silver chloroperiridite—the change proceeds more quickly in hot soln.; C. Karmrodt and E. Uhrlaub, by adding silver nitrate to a soln. of the corresponding sodium salt; J. Lang, by adding silver nitrate to a boiling soln. containing barium chloronitritoperiridate. The rhombohedral crystals of silver chloroperiridite are insoluble in water and acids, and freely soluble in aq. ammonia. When the precipitated silver chloroperiridite is treated with ammonia, M. Delépine observed that it passes into **silver hexamminochloroperiridite,** $Ag_3Ir(NH_3)_6Cl_6$, which loses ammonia on exposure to air or when warmed; and he found that a soln. of iridium trichloride with silver nitrate gives a precipitate of $IrCl_3.AgOH$.

J. Lang boiled barium chloroiridate with barium nitrate, and obtained white **barium nitritochloroperiridite,** $Ba_3(IrCl_6)_2.Ba_3\{Ir(NO_2)_6\}_2$, which is sparingly soluble in cold, more soluble in boiling water. This salt was also prepared by O. W. Gibbs. C. Claus obtained **mercurous chloroperiridite,** Hg_3IrCl_6, as a pale ochre-yellow precipitate, by adding mercurous nitrate to a soln. of potassium chloroperiridite, or chloroiridate. M. Delépine obtained **thallous chloroperiridite,** Tl_3IrCl_6, by boiling the chloroiridate with hydrochloric acid and cooling the liquid. The bronze-coloured lamellæ are re-converted into the chloroiridate by nitric acid.

E. Ogawa tried to prepare **hydrochloroperiridous acid,** H_3IrCl_6, by reducing hydrochloroiridic acid with oxalic acid at 50° to 60° for 40 hrs., but the product was **aquopentachloroperiridous acid,** $H_2[IrCl_5(H_2O)].6H_2O$, in orange-red needles. This acid is dibasic with a degree of ionization 0·65. M. Delépine found that the potassium chloroperiridite is decomposed in aq. soln.: $K_3IrCl_6+H_2O \rightleftharpoons KCl+K_2Ir(H_2O)Cl_5$, and on crystallizing the soln., after the separation of the normal chloroperiridite, needle-like crystals of **potassium aquochloroperiridite,** $K_2Ir(H_2O)Cl_5$, or $K_2[Ir(H_2O)Cl_5]$, are formed—E. Ogawa also obtained this salt in orange-red needles—M. Delépine similarly obtained **rubidium aquochloroperiridite,** $Rb_2Ir(H_2O)Cl_5$, which forms small, thick crystals; **cæsium aquochloroperiridite,** $Cs_2Ir(H_2O)Cl_5$, which forms olive needles; and **ammonium aquochloroperiridite,** $(NH_4)_2Ir(H_2O)Cl_5$, which crystallizes in octahedra. E. Ogawa obtained the monohydrate in orange-red needles. M. Delépine observed that the trimetal salts readily lose their water of crystallization, but the bimetal or aquo-salts undergo no change at 150°. E. Ogawa also prepared **sodium aquochloroperiridite,** $Na_2[Ir(H_2O)Cl_5].6H_2O$, in acicular crystals.

According to M. Delépine, **potassium pentachloropyridinoperiridite,** $K_2[IrpyCl_5]$, is obtained from potassium aquochloroperiridite, or chloroiridate, by the action of pyridine at 100°. The reddish-brown crystals form orange soln. with water. Chlorine converts it

into the iridic salt. The corresponding **silver pentachloropyridinoperiridite**, $Ag_2[IrpyCl_5]$, is blue; and similarly with **thallous pentachloropyridinoperiridite**, $Tl_2[IrpyCl_5]$. By heating the chloroiridate or aquochloroperiridite with pyridine for a longer time at 100°, **potassium tetrachlorobispyridinoperiridate**, $K[Irpy_2Cl_4]$, is formed. There are two isomerides—one orange-yellow, and the other red. The alkali salts are very stable, and the pyridine is not driven out by sulphuric acid at 100°; hydrogen dioxide is without action; and when oxidized with nitric acid or chlorine, iridic tetrachlorobispyridine is produced. Chromic acid has no action. Similarly with **silver tetrachlorobispyridinoperiridite**, $Ag[Irpy_2Cl_4]$; orange crystals of **silver pentachloropyridinodiamminoperiridite**, $Ag_2[IrpyCl_5](NH_3)_2.H_2O$, are formed when the silver salt is dissolved in aq. ammonia. Amorphous **mercurous pentachloropyridinoperiridite**, $Hg_2[IrpyCl_5]$; **mercuric pentachloropyridinoperiridite**, $Hg[IrpyCl_5]$; and **thallous tetrachlorobispyridinoperiridite**, $Tl[Irpy_2Cl_4]$; and **pyridinium tetrachlorobispyridinoperiridite**, $(C_5H_6N)[Irpy_2Cl_4]$, are insoluble in water.

L. N. Vauquelin, and J. J. Berzelius prepared **iridium tetrachloride, or iridic chloride,** $IrCl_4$, by passing chlorine through water in which ammonium chloroiridate is suspended—avoiding the formation of nitrogen chloride—or it can be formed by the action of aqua regia on the same salt or on iridium trichloride. C. Claus, F. Korten, and E. Rimbach and F. Korten employed a similar process. J. J. Berzelius, and C. Claus also prepared the salt by dissolving iridium black, or iridium dioxide in hydrochloric acid; the soln. is evaporated, and any trichloride is converted into the tetrachloride by the addition of aqua regia. F. Krauss and H. Gerlach were unable to prepare the tetrachloride by these methods. N. K. Pscheuitsin and C. E. Krasikoff obtained it by the action of chlorine on ammonium chloroiridate. According to S. Streicher, and L. Wöhler and S. Streicher, the tetrachloride can be obtained by the direct union of the elements at 60° in the presence of liquid chlorine under a press. of 20 atm. for 5 days—at 15°, and 8 atm. press., the conversion required about a year. T. Oppler treated crystals of potassium chloroiridate with hydrofluosilicic acid, at a gentle heat, filtered the soln. after it had stood for 12 hrs., and evaporated the liquid.

The product obtained by evaporating the soln. in vacuo is a dark brown, amorphous mass which is very hygroscopic. P. Vinassa studied the mol. vol. W. D. Treadwell and M. Zürcher studied the electrometric titration of H_2IrCl_6. T. Thomson obtained tetrahedral crystals containing some water, which is expelled along with hydrogen chloride when the salt is heated; at a higher temp., iridium remains. J. H. Gladstone found that a 7·9 per cent. aq. soln. has a mol. refraction of 79·3 for the D-line. S. M. Karim and R. Samuel studied the absorption spectrum. H. G. Grimm studied the salt. D. M. Bose and H. G. Bhar studied the magnetic properties.

The salt is freely soluble in water. C. Brunner said that hydrogen partially reduces the aq. soln. to trichloride. According to J. J. Berzelius, the conc. aq. soln. is oily, and almost black, it appears yellowish-red in thin layers by transmitted light; on dilution, its liquid becomes brownish-red, reddish-yellow, and finally, with a large proportion of water, yellow. According to C. Claus, the dil. soln. contains hypochlorous acid and iridium trichloride. When the aq. soln. is boiled it gives off chlorine. T. Thomson found no decolorization of the soln. occurs with hydrochloric acid, but C. Claus, and H. Rose observed that potassium iodide reduces the aq. soln. H. Rose, and C. Claus observed that hydrogen sulphide decolorizes the aq. soln., and afterwards forms a brown precipitate of iridium sulphide; and similarly with ammonium sulphide in which case the precipitate is soluble in an excess of the reagent. T. Thomson, and E. Frémy observed that the soln. is reduced by sulphurous acid, but not by sulphuric acid. G. Sailer observed that sodium hyposulphite furnishes sodium sulphitoiridate. S. Tennant said that the liquid becomes purple-red when ammonia is added. L. N. Vauquelin, T. Thomson, C. Claus, and H. Rose found that ammonia decolorizes the soln., forming a brown precipitate, but a little iridium remains in soln. without colouring the liquid. H. Rose observed that if the colourless liquid be exposed to air, or boiled to drive off the ammonia, the colourless liquid becomes blue, and deposits a blue powder. O. W. Gibbs observed that potassium nitrite decolorizes the soln. T. Thomson

found that nitric acid exerts no decolorizing action. F. C. Phillips observed that hydrocarbons—ethylene, propylene, isobutylene, and trimethylene—have no action on soln. of iridium tetrachloride; but with boiling soln., reduction slowly occurs with acetylene, and allylene; reduction slowly occurs with carbon monoxide. S. P. Sadtler obtained a complex with ethylene. J. J. Berzelius, and C. Claus observed that when the soln. in alcohol is evaporated, an ethereal odour appears, and iridium trichloride is formed. H. Rose found that sodium formate reduces the hot soln. T. Thomson observed no reducing action with oxalic, tartaric, citric, and acetic acids; H. Rose, and M. C. Lea found that oxalic acid does decolorize the soln. after it has stood for some time; and J. Fiedler observed reduction to iridium occurs in light. C. Claus, S. Tennant, and T. Thomson said that tincture of galls, gallic acid, potassium cyanide, and ferrocyanide reduce the soln., but N. W. Fischer observed no perceptible action with sodium ferrocyanide, and with gallic acid. F. Wöhler and A. Mucklé studied the decolorizing action of potassium cyanide; and C. Claus, that of potassium thiocyanate.

S. Tennant, and T. Thomson said that most of the metals—tin, zinc, iron, etc.—decolorize the aq. soln. of the tetrachloride, and then precipitate some iridium, but not so with gold, or platinum. According to H. Rose, an excess of a soln. of potassium hydroxide produces a scanty blackish-grey precipitate, and the colourless or pale green liquid undergoes little change of colour when heated, but if afterwards allowed to stand for a time, it gradually acquires a darker violet-blue colour, and the change proceeds from above downwards. If the soln. be evaporated it yields a blue precipitate; the dry residue is greenish-white. The reaction was studied by C. Claus. Sodium carbonate decolorizes the soln. without giving a precipitate, and potassium carbonate gives a dark reddish-brown precipitate which gradually redissolves leaving only a trace of a dark brown powder; the colourless soln. so formed does not become blue on standing, but if evaporated to dryness and treated with water it furnishes a blue powder. Potassium hydrocarbonate, and sodium phosphate decolorize the soln. after a while, without producing a precipitate. C. Claus found that sodium hydrophosphate, and borax act like potash lye. T. Thomson observed that the soln. is decolorized by potash and soda lye, and also by barium carbonate, and by calcium carbonate. T. Thomson said that the soln. is not decolorized by copper sulphate; C. Claus, that silver nitrate forms an indigo-blue precipitate which becomes paler and finally colourless; T. Thomson, that zinc sulphate decolorizes the soln.; H. Rose, and T. Thomson that mercurous nitrate gives a pale brown precipitate; T. Thomson, S. Tennant, and H. Rose, that the soln. is decolorized by tin and a pale brown precipitate is formed; T. Thomson, that ferric sulphate does not decolorize the soln.; L. N. Vauquelin, and T. Thomson, that ferrous sulphate decolorizes the soln., producing, according to H. Rose, a dingy green precipitate, or, according to N. W. Fischer, a white one; O. W. Gibbs, that cobaltic hexamminochloride gives a brownish-yellow precipitate; and O. W. Gibbs observed that probably complex salts are formed when iridium chloride is treated with ammonium molybdate or sodium tungstate. L. N. Vauquelin noted that when the iridic salt is mixed with a lower iridium chloride there is a sequence of colour changes—blue, green, violet, etc. The chloropentammines in soln. give a precipitate of the chloride with 20 per cent. hydrochloric acid; a precipitate of the chloronitrate with 30 per cent. nitric acid. With silver nitrate, the chloropentammines give no precipitate in cold or hot soln.; potassium iodide, a yellowish-white precipitate of the chloroiodide; hydrofluosilicic acid, a white precipitate of the chlorofluosilicate; ammonium oxalate (1 : 24), a white precipitate of chloroxalate; potassium dichromate, a yellow precipitate; barium dithionate, a white precipitate of chlorodithionate; sodium phosphate (1 : 10), no precipitate; sodium pyrophosphate (1 : 20), no precipitate; mercuric chloride (1 : 20), a white precipitate; mercuric cyanide, no precipitate; potassium iodomercurate, a white precipitate; potassium ferrocyanide (1 : 20), no precipitate; potassium ferricyanide (1 : 20), a pale yellow precipitate after 12 hrs.; gold chloride,

a garnet-red precipitate; iridium trichloride, a brownish-yellow precipitate; potassium chloroiridate, a chocolate-brown precipitate; platinic chloride, an orange-yellow precipitate; platinic chloride and dil. sulphuric acid, an orange-yellow precipitate; and sulphurous acid had no perceptible action on cold or hot soln. M. Skoblikoff prepared **iridic dichlorotetramminochloride,** $[Ir(NH_3)_4Cl_2]Cl_2$, by adding an excess of conc. hydrochloric acid to a soln. of the dichlorotetrammino-nitrate. It crystallizes from boiling aq. soln. in violet octahedra. Silver nitrate precipitates from the aq. soln. only half the combined chlorine.

According to M. Delépine, when potassium tetrachlorobispyridinoperiridite is treated with chlorine, or nitric acid, there are formed crystals of **iridium tetrachlorobispyridine,** $[Irpy_2Cl_4]$; and A. Gutbier and D. Hoyermann found that pyridine alcoholic soln. reacts with iridium chloride, forming iridium bispyridinotetrachloride, but in hydrochloric acid soln., pyridinium chloroiridate is formed. According to M. Delépine, if the orange-coloured salt be originally employed, the crystals show a green and reddish-violet dichroism in polarized light, and represent the *cis*-form isomorphous with the corresponding platinic salt. The tetrachlorobispyridine reacts with potassium iodide to form iodine and potassium tetrachlorobispyridinoperiridite. M. Delépine and J. Pineau obtained complexes of this salt with $[Ir(NH_3)_3(H_2O)py_2].6H_2O$, and with $[Ir(NH_3)_4pyCl]$. M. Guillot prepared **iridium tetrachlorobispicoline,** $[Ir(C_6H_7N)_2Cl_4]$. B. E. Dixon obtained **iridic chloropentamminohydroxide,** $[Ir(NH_3)_5Cl](OH)_2.H_2O$, by the action of silver oxide on the corresponding chloride; he also prepared **iridic hydroxypentamminochloride,** $[Ir(NH_3)_5(OH)]Cl_2.H_2O$. If potassium pentachloropyridinoperiridite is treated with chlorine, there are formed crystals of **pentachloropyridinoiridic acid,** $H[IrpyCl_5]$, which gives a violet soln. in amyl alcohol. M. Delépine and J. Pineau obtained a complex of this acid with $Ir(NH_3)_4pyCl$. Deep red crystals of **potassium pentachloropyridinoiridate,** $K[IrpyCl_5]$; **rubidium pentachloropyridinoiridate,** $Rb[IrpyCl_5]$; **cæsium pentachloropyridinoiridate,** $Cs[IrpyCl_5]$; **ammonium pentachloropyridinoiridate,** $NH_4[IrpyCl_5]$; and **sodium pentachloropyridinoiridate,** $Na[IrpyCl_5].nH_2O$. The alkali and ammonium salts give precipitates with aq. soln. of silver, mercurous, mercuric, and thallous salts, but not so with lead salts; there are thus formed **silver pentachloropyridinoiridate,** $Ag[IrpyCl_5]$, crystallizing in slender violet needles; **mercurous pentachloropyridinoiridate,** $Hg[IrpyCl_5]$; **mercuric pentachloropyridinoiridate,** $Hg[IrpyCl_5]_2$; and **thallous pentachloropyridinoiridate,** $Tl[IrpyCl_5]$. All these salts are very stable towards acids, but lose pyridine when heated with hydrochloric acid in sealed tubes at 150° to 160°, and the corresponding hexachlorides are formed. A. Gutbier and D. Hoyermann prepared **iridium bisquinolinotetrachloride,** $\{C_5H_4(C_4H_4)N\}_2IrCl_4$; and **iridium bis-α-picolinotetrachloride,** $\{C_5H_5(CH_3)N\}_2IrCl_4$. M. Guillot prepared **picolinium pentachloropicolinoiridate,** $(C_6H_8N_2)_2[Ir(C_6H_7N)Cl_5]$; **silver pentachloropicolinoiridate,** $Ag_2[Ir(C_6H_7N)Cl_5]$; and **thallous pentachloropicnoiridate,** $Tl_2[Ir(C_6H_7N)Cl_5]$.

S. Nagami reported **hydrochloroiridic acid,** H_2IrCl_6, analogous to hydrochloroplatinic acid, to be formed by dissolving iridium dioxide—from 50 grms. of potassium chloroiridate—in hydrochloric acid, and concentrating the soln. in a current of chlorine to prevent reduction. About 40 grms. of reddish-black crystals of hydrochloroiridic acid were formed. The deliquescent crystals are triclinic. The acid is of about the same strength as hydrochloric acid. Migration measurements show that $IrCl_2''$ are present, and no Cl′-ions. Observation on the hydrolysis of acetates, and the eq. conductivity, the depression of the f.p., and the ionic mobilities show that for soln. of concentration less than $0{\cdot}05N$-H_2IrCl_6 ionization proceeds $H_2IrCl_6 \rightleftharpoons 2H^{\cdot}+IrCl_6''$. The eq. conductivities, λ, for soln. with an eq. of the acid in v litres, at 25°, are:

v . . .	10	50	100	1,000	10,000
λ . . .	343·5	380·1	386·9	405·1	417

F. Korten noted that iridic chloride has a smaller tendency to form complex salts than is the case with the corresponding platinic chloride. M. Delépine and P. Boussi studied the dehydration of the chloroiridates, but observed no evidence of the presence of polymerized water molecules. L. N. Vauquelin obtained **potassium chloroiridate,** K_2IrCl_6, from a mixed soln. of iridic and potassium chlorides; and J. J. Berzelius, by passing chlorine over a gently heated mixture of potassium chloride and finely-divided iridium; dissolving the dark brown mass in hot water, adding aqua regia to oxidize any iridium trichloride, evaporating to dryness,

extracting potassium chloride by small quantities of cold water, extracting the residue with boiling water, adding a little aqua regia, and evaporating for crystallization. The extraction with cold water, etc., may be repeated. F. Korten, and E. Rimbach and F. Korten, also obtained the salt by boiling the ammonium salt with potash lye ; and M. Delépine, by double decomposition of the sodium salt and potassium chloride. The reddish-black octahedral crystals are isomorphous with those of the corresponding salts of platinum, palladium, and osmium. L. N. Vauquelin observed that the salt decrepitates when heated; and J. J. Berzelius said that at a higher temp. potassium chloroperiridite is formed, and at a still higher temp., L. N. Vauquelin obtained a mixture of iridium and potassium chloride. According to G. Gire, the potassium salt, K_2IrCl_6, begins to dissociate at 575°, and the heat of the reaction below 774°, the m.p. of potassium chloride, is 36·1 Cals., and above that temp., 41·2 Cals. The vap. press., p, in mm. of mercury, is :

	574°	600°	651°	706°	751°	808°	844°
p . . .	9·2	14·6	30·7	83·0	189	541	933

and the press. in the system : $2K_2IrCl_6+2KCl \rightleftharpoons 2K_3IrCl_6+Cl_2$ are :

	480°	503°	552°	603°	650°	705°	736°	795°
p . . .	3·8	8·3	24·3	67·9	163	437	828	1610

F. Wöhler heated it to volatilize the alkali chloride, and obtained a scaly " skeleton " of iridium. J. J. Berzelius also noted that a mixture of iridium and alkali chloride is formed by heating the salt in hydrogen. S. Nagami found the eq. electrical conductivities, λ, of a soln. of an eq. of the salt in v litres, at 25°, are :

v	100	250	500	1000
λ	125·74	131·75	135·65	138·75

I. V. Ipatéeff and co-workers observed that at 100° to 103°, with hydrogen under press., iridium is more completely deposited than is the case with the platinum salt (*q.v.*) ; and in cases of incomplete precipitation, a blue, colloidal soln. of iridium is produced. L. N. Vauquelin observed that the salt dissolves sparingly in cold water, and that 100 parts of boiling water dissolve 6·7 parts of the salt. The conc. soln. in boiling water is deep red, but in thin layers it is yellow. J. J. Berzelius observed that the salt is insoluble in water saturated with calcium chloride, and in alcohol. Alcohol, or alcohol with potassium chloride in soln., precipitates the salt as a dark red powder from its aq. soln. The salt is less soluble in water containing hydrochloric acid than it is in water alone. C. Claus observed that the aq. soln. decomposes partially when boiled, forming potassium chloroperiridite. E. Leidié observed that when the soln. is heated to 440° in a current of hydrogen chloride, insoluble iridium trichloride, and soluble chloroperiridite are formed. G. Gore said that the salt is insoluble in liquid ammonia. S. P. Sadtler obtained a complex with ethylene. L. N. Vauquelin observed that when treated with an aq. soln. of potassium hydroxide, the yellow soln. becomes colourless in light, but afterwards turns purple, violet, and finally blue. F. Korten, and E. Rimbach and F. Korten prepared **rubidium chloroiridate,** Rb_2IrCl_6, by mixing soln. of iridium tetrachloride and rubidium chloride. The deep red crystals which are precipitated dissolve sparingly in hot water to form a deep red liquid. M. Delépine obtained the salt by double decomposition of rubidium chloride and sodium chloroiridate, and he said that the colour of the crystals varies from brownish-red to brick-red according to the size of the crystals. By a similar process, M. Delépine prepared **cæsium chloroiridate,** Cs_2IrCl_6, in red crystals, sparingly soluble in water. H. Terrey and H. C. Baker measured the potential of the iridi-iridochloride electrode, and obtained for the heat of oxidation of **sodium chloroiridate,** Na_2IrCl_6, 5·6 Cals.

L. N. Vauquelin obtained **ammonium chloroiridate,** $(NH_4)_2IrCl_6$, by adding ammonium chloride to a soln. of iridium tetrachloride, or of sodium chloroiridate ; M. Delépine also obtained it by double decomposition with sodium chloroiridate,

and ammonium chloride. L. N. Vauquelin said that the reddish-black, octahedral crystals are isomorphous with those of the corresponding platinum salt; and M. Delépine added that large crystals are black and that small ones are red. P. Vinassa studied the mol. vol. S. Nagami found the electrical conductivities of soln. with an eq. of the salt in v litres, at 25°, to be :

v	100	250	500	1000
λ	125·81	131·49	137·16	141·72

According to L. N. Vauquelin, 100 parts of cold water dissolve about 5 parts of the salt, forming a reddish-brown soln.; water containing 1 part of the salt in 40,000 parts is perceptibly yellow. C. Claus noted an increased solubility in hot water. F. Korten, and E. Rimbach and F. Korten found the solubility, S grms. of $(NH_4)_2IrCl_6$ per 100 grms. of soln., at $\theta°$, to be :

θ . . .	14·4°	26·8°	39·4°	52·2°	61·2°	69·3°
S . . .	0·6936	0·8988	1·124	1·583	2·068	2·746

or per 100 grms. of water $S=0·7138-0·004970\theta+0·000406\theta^2$. R. Samuel and co-workers studied the absorption spectra of some complex iridium chlorides. E. H. Archibald and J. W. Kern gave for the solubility, S grms. of $(NH_4)_2IrCl_6$ in 100 grms. of water :

	0·2°	10·0°	25·0°	30·0°	40·0°	50·0°	60°	80°
S . .	0·5661	0·7055	1·0910	1·2066	1·5665	1·9664	2·4567	4·3815

and for soln. with C mol. of NH_4Cl per litre at 20° :

C	2·000	1·000	0·200	0·100
S	0·0027	0·0640	0·0780	0·1793

M. Skoblikoff said that the salt is soluble in dil. hydrochloric acid; C. Claus, that it is insoluble in a cold soln. of ammonium chloride; and J. J. Berzelius, that it is insoluble in alcohol. H. V. Collet-Descotils observed that when the salt is suspended in water, with chlorine, it is decomposed with the evolution of nitrogen and the formation of iridic chloride. E. Leidié observed that when the crystals are heated to 440°, in chlorine, iridium tetrachloride is first formed, and that this then passes into the trichloride. L. N. Vauquelin observed that when the aq. soln. is sat. with aq. ammonia, the yellow soln. becomes colourless when exposed to light, and it then becomes successively purple, violet, and blue.

A. Gutbier and co-workers prepared a number of analogous organic chloroiridates. F. Korten, and E. Rimbach and F. Korten also prepared the pyridinium and anilinium salts; and C. Vincent, the methyl-, dimethyl-, and trimethyl-ammonium chloroiridates : **methylammonium chloroiridate**, $(CH_3.NH_3)_2IrCl_6$, in brownish-red needles; **dimethylammonium chloroiridate**, $\{(CH_3)_2NH_2\}_2IrCl_6$, in reddish-brown, rhombic crystals; **trimethylammonium chloroiridate**, $\{(CH_3)_3NH\}_2IrCl_6$, in small needles; **tetramethylammonium chloroiridate**, $\{(CH_3)_4N\}_2IrCl_6$, in dark red crystals; **benzalmethylammonium chloroiridate**, $(CH_3.NH:CH.C_6H_5)_2IrCl_6$, in dark reddish-brown needles; **benzylmethylammonium chloroiridate**, $(CH_3.NH_2.CH_2.C_6H_5)_2IrCl_6$, in dark reddish-brown needles; **ethylammonium chloroiridate**, $(C_2H_5.NH_3)_2IrCl_6$, in brownish-red plates; **diethylammonium chloroiridate**, $\{(C_2H_5)_2NH_2\}_2IrCl_6$, in brownish-red needles; **triethylammonium chloroiridate**, $\{(C_2H_5)_3NH\}_2IrCl_6$, in small needles; **tetraethylammonium chloroiridate**, $\{(C_2H_5)_4N\}_2IrCl_6$, in dark brownish-red crystals; **benzylammonium chloroiridate**, $(C_7H_7.NH_3)IrCl_6$; **dibenzylammonium chloroiridate**, $\{(C_7H_8)_2NH_2\}_2IrCl_6$; **benzalethylammonium chloroiridate**, $(C_2H_5.NH:CH.C_2H_5)_2IrCl_6$, in dark brown needles; **benzylethylammonium chloroiridate**, $(C_2H_5.NH_2.CH_2.C_6H_5)_2IrCl_6$, in black needles; **n-propylammonium chloroiridate**, $(C_3H_7.NH_3)_2IrCl_6$, in brownish-red needles; **iso-propylammonium chloroiridate**, in brownish-red needles; **dipropylammonium chloroiridate**, $\{(C_3H_7)_2NH_2\}_2IrCl_6$; **tripropylammonium chloroiridate**, $\{(C_3H_7)_3NH\}_2IrCl_6$, in dark brown crystals; **n-butylammonium chloroiridate**, $(C_4H_9.NH_3)_2IrCl_6$, in reddish-brown plates; **iso-butylammonium chloroiridate**, in brownish-red needles; **tri-iso-butylammonium chloroiridate**, $\{(C_4H_9)_3NH\}_2IrCl_6$, in ruby-red crystals; **allylammonium chloroiridate**, $(C_3H_5.NH_3)_2IrCl_6$, in dark reddish-brown needles; **di-iso-amylammonium chloroiridate**, $\{(C_5H_{11})_2NH_2\}_2IrCl_6$, in dark brown needles and plates; **tri-iso-amylammonium chloroiridate**, $\{(C_5H_{11})_2NH\}_2IrCl_6$, in dark brown crystals; **benzylammonium chloroiridate**,

$(C_7H_7.NH_3)_2IrCl_6$, in dark brownish-red plates; **ethylenediammonium chloroiridate,** $(C_2H_4.N_2H_6)IrCl_6$, in brownish-red needles; **propylenediammonium chloroiridate,** $(C_3H_6.N_2H_6)IrCl_6$, in reddish-brown crystals; **pyridinium chloroiridate,** $(C_5H_6N)_2IrCl_6$, in reddish-brown needles; E. Rimbach and F. Korten prepared **pyridinium chloroiridate,** $(C_5H_6N)_2IrCl_6$; and **anilinium chloroiridate,** $(C_6H_8N)_2IrCl_6$. A. Gutbier and co-workers obtained **guanidinium chloroiridate,** $\{C.NH(NH_2)_2H\}_2IrCl_6$, in dark brown plates; **triphenylguanidinium chloroiridate,** $\{(C_6H_5)_3C.N(NH_2)_2H\}_2IrCl_6$, in brown needles; **benzalanilinium chloroiridate,** $(C_6H_5.CH : NH.C_6H_5)_2IrCl_6$, in dark reddish-brown crystals; **p-chloroanilinium chloroiridate,** $(C_6H_4.Cl.NH_2)_2IrCl_6$, in dark brown needles; **m-chloroanilinium chloroiridate** and **p-chloroanilinium chloriridate** were obtained in an impure form; **tribenzylammonium chloroiridate,** $\{(C_6H_5.CH_2)_3NH\}_2IrCl_6$, in dark red needles; **dimethyl-o-toluidinium chloroiridate,** $\{(C_6H_4.CH_3.NH(CH_3)_2\}_2IrCl_6$, in dark red crystals; **ψ-cumidinium chloroiridate,** $\{C_6H_2(CH_3)_3NH_3\}_2IrCl_6$, in dark brown needles; **α-picolinium chloroiridate,** $(C_5H_4.CH_3.NH)_2IrCl_6$, in brownish-red needles; **β-picolinium chloroiridate,** in black needles. M. Guillot also prepared the picolinium salt. A. Gutbier and co-workers reported **lutidinium chloroiridate,** $\{C_5H_3(CH_3)_2NH\}_2IrCl_6$, in dark red needles; **collidinium chloroiridate,** $\{C_5H_2(CH_3)_3NH\}_2IrCl_6$, in black crystals; **piperidinium chloroiridate,** $(C_5H_{10}.NH_2)_2IrCl_6$, in reddish-brown crystals; **quinolinium chloroiridate,** $(C_9H_7.NH)_2IrCl_6$, in black, monoclinic prisms, or brownish-red needles; and **iso-quinolinium chloroiridate,** in bronze needles. A. Benrath prepared **quinine chloroiridate,** $(C_{20}H_{24}O_2N_4)_n.H_2IrCl_6$, where n is 1 or 2; **cinchonine chloroiridate,** $(C_{19}H_{22}ON_2)_nH_2IrCl_6$; **cinchonidine chloroiridate,** $(C_{19}H_{22}ON_2)_nH_2IrCl_6$; **strychnine chloroiridate,** $(C_{21}H_{22}O_2N_2)_2IrCl_6$; and **brucine chloroiridate,** $(C_{23}H_{26}O_4N_2)_2H_2IrCl_6$.

U. Antony prepared **lithium chloriridate,** $Li_2IrCl_6.6H_2O$, by passing dry chlorine over a mixture of finely-divided iridium and dehydrated lithium chloride at 300°, the salt is then extracted with water and crystallized; M. Delépine obtained it by evaporating to dryness over sulphuric acid a cold soln. of theoretical proportions of lithium carbonate and hydrochloroiridic acid, and recrystallizing the product from chlorine water. The large crystals of the *hexahydrate* obtained by M. Delépine were black, and the small crystals by U. Antony were garnet red. When dried at 100°, in dry air, the *dihydrate* is formed. The deliquescent crystals of the hexahydrate are freely soluble in water, and in alcohol; and when the aq. soln. is boiled with a little alcohol, the chloroperiridite is formed. J. J. Berzelius, and E. Uricoechea obtained **sodium chloriridate,** $Na_2IrCl_6.6H_2O$, by heating a mixture of finely-divided iridium and sodium chloride to redness in a current of chlorine, as in the case of the potassium salt; and it is formed when a mixture of iridic and sodium chlorides is evaporated to dryness. The black plates and 4-sided prisms are, according to H. Dufet, triclinic, and they are isomorphous with the corresponding platinic salt. According to L. Wöhler and P. Balz, the complex salt forms above 570°, but over 800°, only bivalent iridium exists. According to E. Ogawa, the vap. press., p mm., of a sat. soln. of the *hexahydrate*, are:

	25°	30°	40°	50°	60°	71·68°	79·13°
p . .	75·32	21·23	36·53	60·34	96·80	161·92	219·04

or $\log p = 8\cdot62250 - 2210\cdot71T$ within this range of temp. No isomer was observed. When air dried at 100° is passed over the hexahydrate, the anhydrous salt, melting at 122·5°, is formed. S. Nagami found the electrical conductivities of soln. with an eq. of $NaHIrCl_6$ in 200, 500, and 1000 litres, at 25°, to be respectively, 488, 503, and 512. L. Wöhler and P. Balz studied the thermal decomposition of the sodium salt, and observed no evidence of the formation of a complex of univalent iridium; the salt is stable below 570°, and completely decomposed at 800°. According to G. Gire, sodium chloroiridate begins to dissociate at 600°, and below 764°, the heat of the reaction is 35·3 Cals., and above that temp., 46·0 Cals. According to J. J. Berzelius, when sodium chloroiridate is heated, a brownish-grey residue appears. The salt is freely soluble in water, and somewhat soluble in alcohol. Ammonium chloride precipitates ammonium chloroiridate from the aq. soln.

According to M. Delépine, the fugitive blue precipitate formed when potassium chloroiridate is added to a soln. of silver nitrate, is **silver chloroiridate,** Ag_2IrCl_6, and when kept either alone, or in the presence of an excess of silver nitrate, it passes into yellow chloroperiridite. J. Lang obtained **barium chloroiridate,** presumably

$BaIrCl_6$, by passing chlorine over a mixture of finely-divided iridium and barium chloride at a red-heat. F. Korten, and E. Rimbach and F. Korten obtained this salt from a mixed soln. of the component chlorides; and similarly with **strontium chloroiridate,** presumably $SrIrCl_6$, and with **calcium chloroiridate,** presumably $CaIrCl_6$. They also obtained **cadmium chloroiridate,** presumably $CdIrCl_6$, in black octahedra, from a soln. of the component salts. E. Uricoechea also prepared **magnesium chloroiridate,** in red prisms, soluble in water. M. Delépine prepared **thallous chloroiridate,** Tl_2IrCl_6, in small, opaque, greenish-blue cubes. It is more stable than the corresponding silver salt. When treated with hydrochloric acid, it forms the chloroperiridite.

A. Benrath and co-workers prepared **chromic hexamminochloroiridate,** $[Cr(NH_3)_6]_2(IrCl_6)_3$; **chromic hexamminohydroxychloroiridate,** $[Cr(NH_3)_6](OH)(IrCl_6)$; **chromic chloropentamminochloroiridate,** $[Cr(NH_3]_5Cl]IrCl_6$; **chromic hydroxyaquotetramminochloroiridate,** $[Cr(NH_3)_4(H_2O)(OH)]IrCl_6$; **chromic dichloroaquotriamminochloroiridate,** $[Cr(NH_3)_3(H_2O)Cl_2]_2IrCl_6$; and a complex with nitron, $(C_{20}H_{16}N_4)_2.H_2IrCl_6$. O. W. Gibbs obtained impure **cobaltic hexamminochloroiridate,** $[Co(NH_3)_6]_2(IrCl_6)_3$, by the action of cobaltic hexamminochloride on iridic chloride. A. Benrath and co-workers prepared this salt and also **cobaltic chloropentamminochloroiridate,** $[Co(NH_3)_5Cl]IrCl_6$; **cobaltic aquopentamminochloriridate,** $[Co(NH_3)_5(H_2O)]_2(IrCl_6)_3$; **cobaltic trisethylenediamminochloroiridate,** $[Coen_3]_2(IrCl_6)_3$; **cobaltic cis-** and **trans-hydroxyaquobisethylenediamminochloroiridate,** $[Coen_2(H_2O(OH)]IrCl_6$, and showed that the alleged water of hydration of these salts is really due to occluded or adsorbed water. They also prepared trihydrated **cobaltic cis-** and **trans-dinitritotetramminochloroiridate,** $[Co(NH_3)_4(NO_2)_2]_2IrCl_6.3H_2O$; **cobaltic cis-dichlorobisethylenediamminochloroiridate,** $[Coen_2Cl_2]_2IrCl_6.4H_2O$, and also **cobaltic trans-dichlorobisethylenediamminochloroiridate,** $[Coen_2Cl_2]_2IrCl_6.H_2O$. They also prepared **cobaltic hexamminohydroxychloroiridate,** $[Co(NH_3)_6](OH)IrCl_6$; **cobaltic cis-dichlorotetramminochloroiridate,** $[Co(NH_3)_4Cl_2]_2IrCl_6$; and **cobaltic nitritoaquotetramminochloroiridate,** $[Co(NH_3)_4(H_2O)(NO_2)]IrCl_6$. J. J. Berzelius noted the tendency of osmium and iridium compounds to unite; and R. Hermann obtained dark brown, octahedral crystals with the composition **potassium chloroiridiosmate,** $2K_2IrCl_6.K_2OsCl_6$, which are probably isomorphous mixtures.

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§ 10. The Iridium Bromides

F. Krauss and H. Gerlach [1] obtained **iridium dibromide,** $IrBr_2$, by heating the tribromide at 440°, and **iridium monobromide,** IrBr, by heating the tribromide at 485°. The tribromide is reproduced by heating the dibromide in a sealed tube with bromine.

According to E. Uricoechea, and C. Birnbaum, bromine does not attack iridium

at 100° in a sealed tube, or at a red-heat. If bromine is passed over a mixture of finely-divided iridium and sodium bromide, a reaction sets in at a red-heat, and after the cold product is treated with water, only a small proportion of the iridium dissolves, forming a blue soln. Iridium is not attacked by a mixture of hydrobromic and nitric acids. The hydrated dioxide dissolves in conc. hydrobromic acid, and when the soln. is evaporated by heat, or over sulphuric acid in vacuo, bromine is given off, and dark greenish-brown, or olive-green six-sided crystals of **iridium tribromide,** $IrBr_3.4H_2O$, are formed along with some blue needles of the tetrabromide. The evaporation of the soln. to dryness decomposes the bromide, and when the mass is extracted with water, and subsequently crystallized, the *tetrahydrate* of the tribromide appears in olive-green prisms, which lose all their water, and becomes dark brown at 100° to 120°, and at a dull red-heat, bromine is given off. The salt is freely soluble in water, but not so in alcohol, or ether. The aq. soln. is green, and it becomes blue when treated with chlorine or nitric acid owing to the formation of the tetrabromide; and when heated with chlorine, the bromine is driven off, and the chloride is formed. If the mother-liquor from which olive-green crystals of the tribromide have separated, be evaporated, it furnishes steel-blue, acicular deliquescent crystals of **tribromoperiridious acid,** $H_3IrBr_6.3H_2O$, or *iridium hydrotribromide*. The blue crystals appear brownish-red by transmitted light. They lose water at 100°, and become opaque and brownish-red; they also melt without losing bromine. At a higher temp. hydrogen bromide and bromine are given off, and finally the metal remains. The crystals are easily soluble in water, alcohol, and ether; they decompose in air rapidly to a brown liquid which reacts acid, and expels carbon dioxide from carbonates to form olive-green periridites. G. Geisenheimer prepared some **iridium phosphobromides,** $IrBr_3.3PBr_3$, partially decomposed by water, and $IrBr_3.2PBr_3$, not easily attacked by water. The complex was studied by M. F. Schurigen, and W. Strecker and M. F. Schurigen.

W. Palmaer prepared **iridium hexamminobromide,** $[Ir(NH_3)_6]Br_3$, by crystallization from a soln. of the corresponding nitrate. The six-sided prisms resemble the chloride. The sp. gr. of the salt is 2·942 at 15·5°; and the mol. vol. is 181·9. Similar chromic, cobaltic, and rhodium salts are known. One part of the salt dissolves in 28 to 30 parts of water at room temp. A. Werner and A. P. Smirnoff prepared the lævo-form of **iridium bisethylenediaminobromide,** $[Iren_3]Br_3.3H_2O$, with a sp. rotation of −50° for Na-light. W. Palmaer prepared **iridium aquohexamminobromide,** $[Ir(H_2O)(NH_3)_5]Br_3$, by a method analogous to that used for the chloride. Similar cobaltic, rhombic, and rhodium salts are known. The sp. gr. of the salt is 3·022 at 20°/4°; and the mol. vol., 177·4. One part of the salt dissolves in 4 parts of water at room temp. If the chloropentamminosulphate is treated with the proportion of barium bromide, **iridium chloropentamminobromide,** $[Ir(NH_3)_5Cl]Br_2$, is formed in pale yellow crystals; the rhombic crystals have the axial ratios $a:b:c=0·98765:1:1·5296$; W. Biltz gave for the sp. gr., 3·007 at 16°/4°; and mol. vol., 157·5. Similar chromic and cobaltic salts are known. The salt is soluble in water—1 part of the salt dissolves in 214 parts of water at 15°. If the chloropentamminochloride is boiled with potassium hydroxide for about 5 hrs., and then treated with an excess of 50 per cent. hydrobromic acid, a white crystalline precipitate of the aquopentamminobromide is formed, and when a soln. of this salt is heated, it forms **iridium bromopentamminobromide,** $[Ir(NH_3)_5Br]Br_2$, in yellow, rhombic prisms with the axial ratios $a:b:c=0·9752:1:1·5687$; W. Biltz gave for the sp. gr., 3·245 at 16·5°; and mol. vol., 159·7. Similar chromic, cobaltic, and rhodium salts are known. The salt is soluble in water—1 part of the salt dissolves in 352 parts of water at 12·5°. A. B. Lamb and L. T. Fairhall observed that the speed of the transformation of the bromo-salt to the aquo-salt, at 95°, is in accord with values for unimolecular reactions; and with soln. having 0·00093, 0·0038, and 0·0157 mol per litre, the percentages of aquo-salt present with equilibrium are, respectively, 30·8, 9·6, and 6·3; and at 80°, for 0·00385*M*-soln., 12·6 per cent. According to W. Palmaer, the bromopentammines give a

precipitate of the bromopentamminobromides with the hydrobromic acid ; a precipitate with barium dithionate ; no precipitate with sodium pyrophosphate or with potassium ferricyanide ; and a brownish-yellow crystalline precipitate with iridium trichloride. When conc. hydrobromic acid is added to a warm soln. of the dichlorotetramminochloride, crystals of **iridium dichlorotetramminobromide,** $[Ir(NH_3)_4Cl_2]Br.H_2O$, separate out, and when they are recrystallized from hot water, they form yellow needles or prisms. The *monohydrate* loses its water at 80°. A. Werner and O. de Vries prepared **iridium dinitritotetramminobromide,** $[Ir(NH_3)_4(NO_2)_2]Br.H_2O$, in colourless flat prisms ; and the racemic form of **iridium dinitritobisethylenediaminobromide,** $[Iren_2(NO_2)_2]Br$, in colourless needles—this was resolved into the *dextro-salt*, with a sp. rotation of 26°, and the *lævo-salt* with a sp. rotation of −26° for Na-light. M. Delépine and J. Pineau prepared **iridium chlorobispyridinotriamminobromide,** $[Ir(NH_3)_3py_2Cl]Br_2.H_2O$; and M. Delépine, **iridium dichlorobispyridinodiamminobromide,** $[Ir(NH_3)_2py_2Cl_2]Br.H_2O$.

According to C. Birnbaum, **potassium bromoperiridite,** $K_3IrBr_6.3H_2O$, is produced when finely-divided potassium bromoiridate is triturated with sulphurous acid until the liquid is saturated with salt, warmed on a water-bath until the smell of sulphur dioxide has disappeared, neutralized with potassium carbonate, mixed with potassium bromide, and evaporated for crystallization. It is also obtained by reducing iridium tetrachloride to the trichloride with hydrogen sulphide, and the filtered liquid neutralized with potassium carbonate, then mixed with an excess of potassium bromide, and evaporated for crystallization. The olive-green, 4-sided needles of the *trihydrate* effloresce in air ; and at 100° to 120°, lose all their water and become pale brown. Iridium and potassium bromide remain when the salt is ignited. Alkali lye precipitates green hydrated hemitrioxide from an aq. soln. of the salt ; chlorine, and nitric acid colour the aq. soln. blue owing to the formation of the bromoiridate. C. Birnbaum prepared **ammonium bromoperiridite,** $(NH_4)_3IrBr_6.\frac{1}{2}H_2O$, by a method analogous to that employed for the potassium salt. The olive-brown needles of the *hemihydrate* lose water at 100°, and become brown, and when calcined iridium remains. The salt is sparingly soluble in cold water, and readily soluble in hot water. A mixed soln. of sodium bromide and iridium tribromide furnishes dark olive-green rhombohedra of **sodium bromoperiridite,** $Na_3IrBr_6.12H_2O$, which effloresce in air. The dodecahydrate melts at 100°, loses all its water at 150°, and becomes brownish-yellow ; and when ignited, forms iridium and sodium bromide. Chlorine, and nitric acid turn the greenish-yellow aq. soln. blue. The addition of silver nitrate to a soln. of potassium bromoperiridite precipitates silver bromoperiridite, Ag_3IrBr_6, as a dirty-green, amorphous mass insoluble in water and acids. The freshly-prepared salt is soluble in aq. ammonia ; the dried salt is only partially soluble. E. Uricoechea made some observations on this salt.

According to C. Birnbaum, **iridium tetrabromide** or **iridic bromide,** $IrBr_4$, is obtained by dissolving hydrated iridium dioxide in cold hydrobromic acid ; and by treating potassium bromoiridate with hydrofluosilicic acid, and after the mixture has stood for 24 hrs., filtering off the potassium fluosilicate. The aq. soln. decomposes when evaporated, forming the tribromide and hydrotribromide ; if evaporated with conc. nitric acid, to prevent reduction, a blue crystalline mass is formed which is freely soluble in water and alcohol ; and which furnishes iridium when ignited. If hydrated iridium dioxide is heated to 300° in a sealed tube with bromine, G. Geisenheimer observed that black needles of **iridium dioxyoctobromide,** $2IrBr_4.IrO_2$, are formed. G. Geisenheimer prepared a complex **iridic phosphochlorobromide,** $IrBr_4.2PCl_3$.

F. Krauss and H. Gerlach observed that iridium tetrahydroxide reacts with hydrogen bromide at ordinary temp., forming **iridium aquohydroxydibromide,** $[Ir(H_2O)(OH)Br_2].2H_2O$; and when the *dihydrate* is heated, it forms the anhydrous salt which, when dissolved in water, forms **dibromodihydroxyiridic acid,** $H[Ir(OH)_2Br_2]$. When the aquohydroxydichloride is treated with hydrogen

bromide, it yields **iridium aquotribromide,** $[Ir(H_2O)Br_3]$, which cannot be dehydrated without decomposition; it yields the dibromide at 440°, and the monobromide, at 485°. J. P. Mathieu studied the absorption spectrum of **iridium trisethylenediaminobromide,** $[Ir\ en_3]Br_3.2H_2O$.

C. Birnbaum prepared **potassium bromoiridate,** K_2IrBr_6, by mixing conc. soln. of potassium bromide and iridium tetrabromide, and evaporating over sulphuric acid in vacuo; by triturating a mixture a conc. soln. of potassium bromide, and ammonium bromoiridate on a water-bath and then cooling the soln.; and by adding a conc. soln. of potassium bromide to a warm, conc. soln. of sodium chloroiridate, and recrystallizing the salt by cooling a hot aq. soln. A. Gutbier and M. Riess prepared the alkali salts in blue octahedra by adding the alkali bromides to a soln. of iridium hydroxide in hydrobromic acid. According to C. Birnbaum, the salt forms black octahedra belonging to the cubic system; the salt is stable in air, and at dull redness it forms iridium and potassium bromide. It is sparingly soluble in cold water, and freely soluble in hot water; it is not soluble in alcohol and ether; chlorine water slowly converts it into the corresponding chloroiridate; an aq. soln. of silver nitrate gives a dirty green precipitate; aq. soln. of sodium chloride or sulphate, and of barium chloride give no precipitates in the cold, but when heated, some bromine is set free. A. Gutbier and M. Riess prepared **rubidium bromoiridate,** Rb_2IrBr_6, and **cæsium bromoiridate,** Cs_2IrBr_6, in blue octahedra. If an aq. soln. of iridium chloride be treated with sodium bromide, and nitric acid, and then evaporated, colourless plates of sodium bromide, rhombohedra of sodium nitrate, and black needles of **sodium bromoiridate,** $Na_2IrBr_6.nH_2O$, are formed. The latter become pale blue when dried; and on ignition yield a mixture of sodium bromide, and iridium. The salt dissolves in water, and in alcohol, and is reduced on evaporating the soln. A. Gutbier and M. Riess prepared this salt. E. Uricoecha made some observations on this salt. By triturating powdered ammonium chloroiridate with a soln. of sodium bromide, heated on a water-bath, and cooling the liquid, dark blue, octahedral crystals of **ammonium bromoiridate,** $(NH_4)_2IrBr_6$, free from sodium, are formed. Ammonium bromoiridate resembles the corresponding potassium salt, but it is less soluble in cold water; with a little soda lye, some periridite is formed, with much soda, hydrated oxide is formed. A. Gutbier and M. Riess also prepared the ammonium salt.

A. Benrath prepared a number of complex bromoiridates—*e.g.* **chromic hexamminobromoiridate,** $[Cr(NH_3)_6]_2(IrBr_6)_3$; **chromic hexamminonitratobromoiridate,** $[Cr(NH_3)_6](NO_3)IrBr_6$; **chromic hexamminosulphatobromoiridate; cobaltic hexamminobromoiridate,** $[Co(NH_3)_6]_2(IrBr_6)_3$; **chromic chloropentamminobromoiridate,** $[Cr(NH_3)_5Cl]IrBr_6$; **cobaltic hexamminonitratobromoiridate;** and **cobaltic hexamminosulphatobromoiridate; cobaltic aquopentamminobromoiridate,** $[Co(NH_3)_5(H_2O)]_2(IrBr_6)_3$; **cobaltic aquopentamminochlorobromoiridate,** $[Co(NH_3)_5(H_2O)]Cl(IrBr_6)$ and $[Co(NH_3)_5(H_2O)]_2Cl_4(IrBr_6)$; **cobaltic aquopentamminosulphatobromoiridate,** $[Co(NH_3)_5(H_2O)]_4(SO_4)_3(IrBr_6)_3$; **cobaltic diaquotetramminosulphatobromoiridate,** $[Co(NH_3)_4(H_2O)_2]_2SO_4(IrBr_6)_2)$; **cobaltic chloropentamminobromoiridate,** $[Co(NH_3)_5Cl]IrBr_6$; **cobaltic sulphatopentamminobromoiridate,** $[Co(NH_3)_5SO_4]_2IrBr_6$; **cobaltic sulphatopentamminosulphatobromoiridate,** $[Co(NH_3)_5SO_4]_4(SO_4)(IrBr_6)$; **cobaltic nitritoaquopentamminobromoiridate,** $[Co(NH_3)_4(H_2O)(NO_2)]IrBr_6$; **cobaltic hydroxyaquotetramminosulphatobromoiridate,** $[Co(NH_3)_4(H_2O)(OH)]_2(SO_4)IrBr_6$; **cobaltic dinitritotetramminobromoiridate,** $[Co(NH_3)_4(NO_2)_2]_2IrBr_6$, in its cis- and trans-forms; and **cobaltic carbonatotetramminobromoiridate.**

A. Gutbier and M. Riess prepared some salts with organic bases. Thus, **methylammonium bromoiridate,** $(CH_3NH_3)_2IrBr_6$, forms dark blue octahedra; **dimethylammonium bromoiridate,** $\{(CH_3)_2NH_2\}_2IrBr_6$, in dark blue needles; **trimethylammonium bromoiridate,** $\{(CH_3)_3NH\}_2IrBr_6$, in dark blue needles; **ethylammonium bromoiridate,** $(C_2H_5.NH_3)_2IrBr_6$, in dark blue plates; **diethylammonium bromoiridate,** $\{(C_2H_5)_2NH_2\}_2IrBr_6$, in dark blue, monoclinic prisms; **triethylammonium bromoiridate,** $\{(C_2H_5)_3NH\}_2IrBr_6$, in dark blue plates; **n-propylammonium bromoiridate,** $(C_3H_7.NH_3)_2IrBr_6$, in dark blue, six-sided plates; **iso-**

propylammonium bromoiridate, in dark blue needles; **n-butylammonium bromoiridate**, $(C_4H_7.NH_3)_2IrBr_6$, in dark blue, six-sided plates; **iso-butylammonium bromoiridate**, in dark blue plates; **ethylenediammonium bromoiridate**, $(C_2H_4.N_2H_6)IrBr_6$, in dark blue, cubical crystals; and **propylenediammonium bromoiridate**, $(C_3H_6.N_2H_6)IrBr_6$, in deep blue prisms; A. Gutbier and B. Ottenstein obtained **o-bromoanilinium chloroiridate**, $(C_6H_4.Br.NH_3)_2IrCl_6$; **m-bromoanilinium chloroiridate**, in dark brown needles; and **p-bromoanilinium chloroiridate**, in dark reddish-brown needles. A. Gutbier and M. Riess obtained **pyridinium bromoiridate**, $(C_5H_5.NH)_2IrBr_6$, in deep blue plates; **α-picolinium bromoiridate**, $\{C_5NH_5(CH_3)\}_2IrBr_6$, in dark blue, six-sided, monoclinic plates; **quinolinium bromoiridate**, $(C_9H_7NH)_2IrBr_6$, in dark blue needles; and **benzylammonium bromoiridate**, $(C_7H_7.NH_3)_2IrBr_6$, in dark blue, six-sided plates. A. Benrath prepared **quinine bromoiridate**, $(C_{20}H_{24}O_2N_2)_nH_2IrBr_6$, where n is 1 or 2; **cinchonine bromoiridate**, $(C_{19}H_{22}ON_2)_nH_2IrBr_6$; **cinchonidine bromoiridate**, $(C_{19}H_{22}ON_2)_nH_2IrBr_6$; **strychnine bromoiridate**, $(C_{21}H_{22}O_2N_2)_2H_2IrBr_6$; **brucine bromoiridate**, $(C_{23}H_{26}O_4N_2)_2H_2IrBr_6$; and "**nitron**" **bromoiridate**, $(C_{20}H_{16}N_4)_2H_2IrBr_6$.

M. D. Tard prepared **potassium hexabromoiridate**, $K_3[IrBr_6].4H_2O$; **potassium aquopentaboroiridate**, $K_2[Ir(H_2O)Br_5]H_2O$; **rubidium hexabromoiridate**, $Rb_3[IrBr_6].H_2O$; **rubidium aquopentabromoiridate**, $Rb_2[Ir(H_2O)Br_5]$; **cæsium hexabromoiridate**, $Cs_3[IrBr_6].H_2O$; and the more complex salt $Cs_5Ir_3Br_{14}.2H_2O$.

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§ 11. The Iridium Iodides

F. Krauss and H. Gerlach [1] obtained **iridium monoiodide**, IrI, and probably some diiodide by heating the triodide. According to F. Krauss and H. Gerlach, and T. Oppler, finely-divided iridium does not unite directly with iodine even in a sealed tube at 80° to 100°; but if the iridium be mixed with potassium iodide, union occurs at 60°. If sulphur dioxide be passed through the water holding the iridium tetraiodide in suspension, T. Oppler obtained what he considered to be **iridium diiodide**, or **iridous iodide**, IrI_2, but this result has not been confirmed. If finely-divided ammonium iodoiridate be boiled with a conc. soln. of potassium iodide, the deep purple-red liquid deposits a greyish-black powder of **ammonium iodoiridite**, $(NH_4)_2IrI_4$, which does not decompose at 200°. It is insoluble in cold or hot water, and in alcohol; warm dil. acids, and soln. of the alkali iodides dissolve the salt; dil. soln. of alkali carbonates colour the salt green, and, as ammonia is evolved, the colour becomes yellow.

T. Oppler prepared **iridium triiodide**, IrI_3, by mixing an aq. soln. of potassium iodoiridate and ammonium chloride: $2K_2IrI_6+4NH_4Cl=4KCl+I_2+4NH_4I+2IrI_3$. When the precipitate is extracted with alcohol and with water, the triiodide remains as a greenish powder which is sparingly soluble in water, and in alcohol, but more soluble in hot water. The existence of the triiodide has not been confirmed. The evaporation of the mother-liquor obtained in the preparation of the triiodide, furnishes crystals of **ammonium iodoperiridite**, $(NH_4)_3IrI_6.\frac{1}{2}H_2O$, in microscopic needles, which when ignited leave a residue of iridium. The salt is

not soluble in cold water, or alcohol, but it is soluble in hot water. T. Oppler prepared **potassium iodoperiodite,** K_3IrI_6, by treating a soln. of iridium trichloride with a conc. soln. of potassium iodide, and washing the green, crystalline powder. The salt furnishes a residue of iridium and potassium iodide when it is heated; it is not soluble in water, or alcohol; it is dissolved slowly by acids; and readily dissolved by warm alkali lye, the alkali lye does not act in the cold; with a gentle heat, a brown soln. is formed, and with stronger heating, the colourless soln. becomes violet.

W. Palmaer prepared **iridium hexamminoiodide,** $[Ir(NH_3)_6]I_3$, by treating the corresponding hydroxide with an excess of hydriodic acid. The yellow pyramids or plates lose iodine when heated. Similar chromic and cobaltic salts are known. The sp. gr. of the salt is 3·291 at 16·5°/4°; and the mol. vol., 205·4. The salt is freely soluble in water—1 part of the salt dissolves in 91 parts of water at 18°. By the action of hydriodic acid on the corresponding nitrate, **iridium aquopentamminoiodide,** $[Ir(NH_3)_5(H_2O)]I_3$, is formed. The sp. gr. is 3·353 at 14°/4°; and the mol. vol., 201·9. Similar chromic and cobaltic salts are known. One part of the salt dissolves in about 15 parts of water at room temp. V. V. Lebendinsky, and A. Werner and A. P. Smirnoff prepared the dextro-form of **iridium trisethylenediamminoiodide,** $[Iren_3]I_3$, with a sp. rotation of 42° in D-light. According to W. Palmaer, by decomposing a soln. of chloropentamminosulphate with the theoretical proportion of barium iodide, **iridium chloropentamminoiodide,** $[Ir(NH_3)_5Cl]I_2$, is formed in yellowish-brown, rhombic prisms, with the axial ratios $a : b : c = 0·94239 : 1 : 1·4220$; W. Biltz gave for the sp. gr., 3·118 at 15·5°/4°; and mol. vol., 182·0. A similar cobaltic salt is known. The salt is soluble in water—1 part of salt dissolves in 104·5 parts of water at 15°; and **iridium iodopentamminoiodide,** $[Ir(NH_3)_5I]I_2$, is formed by heating the aquopentamminoiodide to 100°. The six-sided prisms, and octahedra belong to the rhombic system, and have the axial ratios $a : b : c = 0·993 : 1 : 1·552$; W. Biltz gave for the sp. gr. 3·586 at 15·5°/4°; and the mol. vol., 183·8. Similar chromic and rhodium salts are known. One part of salt dissolves in 345 parts of water at 14°, and in 50 parts of boiling water. A. B. Lamb and L. T. Fairhall observed that the speed of conversion to the aquo-salt is in accord with the requirements for a unimolecular reaction, and that for equilibrium, at 95°, with soln. having 0·00093 and 0·0038 mol per litre, there are present 47·5 and 13·1 per cent. of the aquo-salt. According to W. Palmaer, fuming hydrochloric acid gives a small crystalline precipitate, and the dil. acid, no precipitate; nitric acid gives a yellowish-white, crystalline precipitate; hydrofluosilicic acid, a precipitate after 24 hrs.; neutral potassium chromate, a precipitate after 24 hrs.; potassium dichromate, an orange-red precipitate; barium dithionate, a precipitate after 24 hrs.; sodium pyrophosphate, no precipitate; mercuric chloride, a white precipitate; potassium iodomercurate, a pale yellow precipitate; potassium ferrocyanide or ferricyanide, no precipitate; gold chloride, a yellowish-brown precipitate; and iridium trichloride, a brownish-yellow precipitate. M. Delépine and J. Pineau prepared **iridium chlorobispyridinotriamminoiodide,** $[Ir(NH_3)_3py_2Cl]I_2.H_2O$; and M. Delépine, **iridium dichlorobispyridinodiamminoiodide,** $[Ir(NH_3)_2py_2Cl_2]I_2$. Yellowish-brown, acicular crystals of **iridium nitritopentamminoiodide,** $[Ir(NH_3)_5(NO_2)]I_2$, have been prepared, and likewise colourless leaflets or prisms of **iridium dinitritotetramminoiodide,** $[Ir(NH_3)_4(NO_2)_2]I$. By adding potassium iodide to an aq. soln. of the corresponding chloride, yellow needles of **iridium dichlorotetramminoiodide,** $[Ir(NH_3)_4Cl_2]I$, are formed. E. Rosenbohm studied the magnetic susceptibility. A. Werner and O. de Vries prepared racemic **iridium dinitritobisethylenediaminoiodide,** $[Iren_2(NO_2)_2]I$.

J. L. Lassaigne boiled an aq. soln. of iridium tetrachloride with potassium iodide, and hydrochloric acid, and obtained a black powder which was shown by T. Oppler to be **iridium tetraiodide, or iridic iodide,** IrI_4. This salt gives off iodine at about 357°, but does not lose weight at 100°; it is insoluble in water, but soluble in a soln.

of potassium iodide. T. Oppler observed that **potassium iodoiridate,** K_2IrI_6, is formed when iodine vapour is passed over a mixture of finely-divided iridium and potassium iodide at 60° to 70°; when an aq. soln. of iridium tetrachloride is poured into a conc. soln. of potassium iodide, and the precipitate washed with cold water; and when a warm soln. of iridium tetraiodide and potassium iodide is cooled. The dark green, octahedral crystals can be dried over calcium chloride; they do not lose weight at 100°; and they are soluble in water, but not in alcohol. The ruby-red aq. soln. is not reduced by hydrogen sulphide in the cold, but when warm, a turbidity slowly appears, and after some hours, the iridium is precipitated as sulphide; ammonium sulphide decolorizes the liquid producing a dark red, flocculent precipitate; and the soln. is reduced by sulphur dioxide. Aq. ammonia gives a pale yellowish-green or yellowish-brown precipitate which forms with an excess of ammonia a lemon-yellow soln., and if the ammonia is expelled by boiling, the liquid becomes colourless without precipitation. Potassium ferrocyanide produces no change with cold soln., but a warm soln. becomes turbid. Soda lye acts on a soln. of the iodide as in the case of the chloride; copper sulphate colours the soln. chestnut-brown, and when it is boiled the colour is green and a black crystalline precipitate is formed; and silver nitrate gives a dark green, almost black, precipitate.

According to F. Krauss and H. Gerlach, iridium tetrahydroxide is not acted on by iodine, but hydrogen iodide forms **iridium aquotriiodide,** $[Ir(H_2O)I_3].2H_2O$; and when the *dihydrate* is heated it loses two mols. of water, and when further heated it forms the diiodide and monoiodide. When the aquotriiodide is dissolved in water, it probably forms **triiodohydroxyiridic acid,** $[H[Ir(OH)I_3]$.

T. Oppler prepared **sodium iodoiridate,** Na_2IrI_6, by the methods employed for the potassium salt, but best, by treating a soln. of iridium tetrachloride with an excess of a conc. soln. of sodium iodide. a dark reddish-brown precipitate of iridium and sodium iodide is formed which becomes dark brownish-green when the salt is ignited. It is not soluble in cold water, but it is sparingly soluble in hot water, and insoluble in alcohol. T. Oppler obtained **ammonium iodoiridate,** probably $(NH_4)_2IrI_6$, by allowing a soln. of finely-divided ammonium chloroiridate in a cold, conc. soln. of potassium iodide, to stand for some weeks. The dark brown crystals decompose when ignited, forming iridium. The salt is freely soluble in water, and it decomposes in aq. soln., and when heated, ammonium iodoiridite and iridium tetriodide are formed. The salt is soluble in acids, and in alkali lye. Alkali lye simultaneously reduces the salt as in the case of the potassium salt. Ammonium iodoiridate is not soluble in alcohol.

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§ 12. The Iridium Ammines

In 1828, J. J. Berzelius [1] obtained some impure, indefinite iridium chloroammines; in 1853, M. Skoblikoff prepared a few definite ammines; in 1854, C. Claus reported some more; and W. Palmaer, between 1889 and 1896, prepared a number of the complex salts and studied them in the light of the co-ordination theory.

A.—*Derivatives of bivalent iridium, with a co-ordination number* 4.

I.—**The tetrammine family,** or compounds of the bivalent, basic group $[IrA_4]''$.
Tetrammines, $[Ir(NH_3)_4]X_2$, represented by (1) chloride; (2) sulphate; and (3) nitrate.

II.—**The triammine family.**

III.—**The diammine family,** or compounds of the null-valent group $[IrA_2X_2]$.
Diammines, $[Ir(NH_3)_2X_2]$, represented by (1) the chloro-salt; and (2) the sulphato-salt.

B.—*Derivatives of tervalent iridium with a co-ordination number* 6.

I.—**The hexammine family,** or compounds of the tervalent basic group: $[IrA_6]'''$.
(i) *Hexammines*, $[Ir(NH_3)_6]X_3$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) iodide; (5) carbonate; and (6) nitrate.
(ii) *Aquopentammines*, $[Ir(NH_3)_5(H_2O)]X_3$, represented by (1) chloride, and a chloroplatinate; (2) bromide; (3) nitrate; and (4) ferrocyanide.
(iii) *Bispyridinotetrammine*, $[Ir(NH_3)_4py_2]X_3$, represented by the chloride.
(iv) *Trisethylenediammines*, $[Iren_3]X_3$, represented by racemic, and dextro- and lævo-forms: (1) bromide; (2) iodide; and (3) camphornitronate.
(v) *Aquobispyridinotriamminochloride*, $[Ir(NH_3)_3py_2(H_2O)]X_3$, represented by the chloride, and by a complex with $[Irpy_2Cl_4]$.

II.—**The pentammine family,** or compounds of the bivalent basic group: $[IrA_5X]''$.
(i) *Hydroxypentammines*, $[Ir(NH_3)_5(OH)]X_2$, represented by (1) the hydroxide; (2) chloride; and (3) nitrate.
(ii) *Chloropentammines*, $[Ir(NH_3)_5Cl]X_2$, represented by (1) hydroxide; (2) chloride, and chloroperiridite; (3) bromide; (4) iodide; (5) sulphate; (6) hydrosulphate; (7) dithionate; (8) chloronitrite; (9) nitrate; and (10) oxalate.
(iii) *Chloropyridinotetrammines*, $[Ir(NH_3)_4pyCl]X_2$, represented by (1) the chloride; (2) chloromercurate; (3) sulphate; (4) dichromate; and (5) picrate; as well as complexes with $[Irpy_2Cl_4]$, and with $[IrpyCl_5]$.
(iv) *Chloroaquobispyridinodiammine*, $[Ir(NH_3)_2py_2(H_2O)Cl]X_2$, represented by the carbonate.
(v) *Chlorotriamminobispyridines*, $[Ir(NH_3)_3py_2Cl]X_2$, represented by (1) the complex with the base $[Irpy_2Cl_4]^{\cdot\cdot}$; (2) chloride; (3) bromide; (4) iodide; and (5) sulphate.
(vi) *Bromopentammines*, $[Ir(NH_3)_5Br]X_2$, represented by (1) bromide; (2) sulphate; and (3) nitrate.
(vii) *Iodopentammines*, $[Ir(NH_3)_5I]X_2$, represented by the iodide.
(viii) *Nitritopentammines*, $[Ir(NH_3)_5(NO_2)]X_2$, represented by (1) chloride; (2) iodide; (3) sulphate; and (4) nitrite.
(ix) *Nitratopentammines*, $[Ir(NH_3)_5(NO_3)]X_2$, represented by (1) nitrate; and (2) chloronitrate.

III.—**The tetrammine family,** or compounds of the univalent basic group: $[IrA_4X_2]$.
(i) *Dichlorotetrammines*, $[Ir(NH_3)_4Cl_2]X$, represented by (1) chloride, and the chloroperiridite; (2) bromide; (3) iodide; and (4) sulphate.
(ii) *Dichlorobispyridinodiammines*, $[Ir(NH_3)_2py_2Cl_2]R$, represented by (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) hydrosulphate; and (6) the complex with the base $[Irpy_2Cl_4]^{\cdot\cdot}$.
(iii) *Dinitritotetrammines*, $[Ir(NH_3)_4(NO_2)_2]X$, represented by (1) chloride; (2) bromide; (3) iodide; (4) sulphate; and (5) nitrite.
(iv) *Dinitritobisethyelenediammines*, $[Iren_2(NO_2)_2]X$, represented by racemic, and dextro- and lævo-forms; (1) bromide; (2) iodide; (3) perchlorate; (4) nitrate; (5) bromocamphor sulphonate; and (6) camphor sulphonate.

IV.—**The triammine family,** or compounds of the null-valent group: $[IrA_3X_3]$.

(i) *Triammines,* $[Ir(NH_3)_3X_3]$, represented by (1) the chloro-salt, and (2) the nitrito-salt.

(ii) *Trispyridines,* $[Irpy_3X_3]$, represented by the cis- and trans-trichloro-salts.

(iii) *Trispicolines,* $[Ir(C_6H_7N)_3X_3]$, represented by the trichloro-salt.

(iv) *Diaquopicolines,* $[Ir(C_6H_7N)H_2O)_2X_3]$, represented by the trichloro-salt.

(v) *Aquobispyridines,* $[Irpy_2(H_2O)X_3]$, represented by (1) hydroxydichloro-salt; and (2) the chloroxalato-salt.

V.—**The diammine family,** or compounds of the univalent basic group: $[IrA_2X_4]^{\cdot}$.

(i) *Tetrachlorobispyridinoperiridites,* $[Irpy_2Cl_4]R$, represented by (1) the potassium, and (2) ammonium salts; and complexes with (3) $[Ir(NH_3)_2py_2Cl_2]$, and (4) $[Irpy_2Cl_4]$.

(ii) *Dioxalatobispyridinoperiridites,* $[Irpy_2(C_2O_4)_2]R$, represented by the potassium salt.

VI.—**The monammine family,** or compounds of the bivalent basic group: $[IrA.X_5]^{\cdot\cdot}$.

Pentachloropyridines, $[IrpyCl_5]R_2$, represented by the acid and the potassium salt.

VII.—**The hexa-acid family,** or the compounds of the tervalent acidic group: $[IrX_6]'''$, represented by the chloro-, bromo-, iodo-, sulphito-, sulphato-, nitrito-, nitrato-, and other periridites.

C.—*Derivatives of quadrivalent iridium, with a co-ordination number* 6.

I.—**The hexammine family.**

II.—**The pentammine family.**

III.—**The tetrammine family,** or compounds of the bivalent acidic group: $[IrA_4X_2]''$.

Dichlorotetrammines, $[Ir(NH_3)_4Cl_2]X_2$, represented by (1) chloride; and (2) sulphate.

IV.—**The triammine family.**

V.—**The diammine family,** or compounds of the null-valent group: $[IrA_2X_4]$.

(i) *Tetrachlorobispyridine,* $[Irpy_2Cl_4]$.

(ii) *Tetrachlorobispicoline,* $[Ir(C_6H_7N)_2Cl_4]$.

VI.—**The monammine family,** or compounds of the univalent basic group: $[IrAX_5]^{\cdot}$.

Pentachloropyridines, $[IrpyCl_5]R$, represented by the acid when R represents $H^{\cdot}$.

VII.—**The hexa-acid family,** or compounds of the bivalent acidic group: $[IrX_6]''$, represented by the chloro-, bromo-, iodo- and other iridates.

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§ 13. The Iridium Sulphides and Sulphates

According to J. J. Berzelius,[1] when iridium is heated in sulphur vapour, it takes up sulphur with a slight incandescence, but part of the metal remains uncombined. R. Böttger, and U. Antony said that **iridium monosulphide,** IrS, is formed when one of the higher sulphides is heated out of contact with air; and J. J. Berzelius obtained it by the action of hydrogen sulphide on an iridous salt,

and washing the precipitate with a soln. of ammonium chloride or an acid to prevent it passing through the filter-paper—as a colloid. H. G. Krall, and L. Wöhler and co-workers observed that at 600°, in nitrogen, the higher sulphides form the monosulphide. According to J. J. Berzelius, when the sulphide is prepared in the dry way, it is dark grey, or bluish-black; and when prepared in the wet way, dark yellowish-brown. J. J. Berzelius observed that the sulphide is not decomposed by ignition in a closed vessel, but when roasted in air, it gives off sulphur dioxide, and leaves a residue of basic sulphate. The sulphide prepared in the dry way is insoluble in nitric acid, and insoluble or sparingly soluble in aqua regia; that prepared by the wet process readily dissolves, even in cold nitric acid, forming a brown sulphate in the cold and not in excess, and an orange-yellow sulphate if the acid be hot and in excess. The precipitated sulphide dissolves in a soln. of potassium sulphide more readily than is the case with the precipitated platinum sulphide. The alleged formation of a reddish-brown soln. with water is due to the formation of a dispersed colloid—*vide supra*. V. N. Ivanoff obtained complexes with this carbamide of variable composition.

According to J. J. Berzelius, and A. Bettendorff, **iridium sesquisulphide,** or **iridium hemitrisulphide,** Ir_2S_3, is formed when a salt of tervalent iridium is treated with hydrogen sulphide. The precipitate is dark brown, or orange-yellow. It does not become acidic when dried, and if heated, it first gives off water and sulphur dioxide, and afterwards sulphur is given off until the monosulphide is formed. It behaves towards nitric acid, and potassium sulphide like the precipitated monosulphide. Its alleged sparing solubility in water to form a yellow soln. is probably due to the dispersion of the colloid, because the dispersion does not occur in the presence of electrolytes.

L. N. Vauquelin reported **iridium disulphide,** or **iridic sulphide,** IrS_2, to be formed by heating ammonium chloroiridate with an equal weight of sulphur; L. R. von Fellenberg, by heating a mixture of finely-divided iridium, sulphur, and alkali carbonate and leaching out the soluble matters with water. R. Böttger obtained it by allowing a soln. of dry iridium tetrachloride, absolute alcohol, and carbon disulphide to stand in a bottle, with frequent agitation, for about a week; the black, gelatinous mass is twice washed with alcohol to remove the carbon disulphide, boiled with a large proportion of water, washed until free from chlorides, pressed between bibulous paper, and dried in vacuo below 125°, over sulphuric acid. J. J. Berzelius reported the disulphide to be formed by passing hydrogen sulphide into an aq. soln. of iridium tetrachloride, or potassium chloroiridate, and, according to L. R. von Fellenberg, washing the precipitate with boiling water, drying it in vacuo, and then heating it in an atm. of carbon dioxide. H. G. Krall, and L. Wöhler and co-workers found that iridium trichloride and dry hydrogen sulphide, at 600°, form the disulphide. U. Antony recommended preparing the disulphide by passing hydrogen sulphide over lithium chloroiridate at 4° to 7°—no action occurs below 0°, and above 10°, the attack is very rapid and free sulphur is formed; the product is repeatedly extracted with absolute alcohol, and dried at 90° to 100° in a current of carbon dioxide.

C. Claus denied the statement that the disulphide is formed by passing hydrogen sulphide through a soln. of a salt of quadrivalent iridium. The iridic salt is reduced wholly or partially to sulphur and a salt of tervalent iridium by the hydrogen sulphide, so that, as proved by U. Antony, the precipitate is a mixture of the hemitrisulphide and the disulphide. U. Antony passed hydrogen sulphide through a 2 per cent. aq. soln. of potassium chloroiridate at 90° to 100°, and observed that a brown precipitate was formed, and the soln. gradually lost its dark colour, but, even after a prolonged exposure to the gas, it still remained reddish-yellow; the precipitate was washed with a soln. of hydrogen sulphide out of contact with air, and dried at 90° in a current of carbon dioxide. The powder did not change in air, it contained no free sulphur, and its composition approximated to that of the mixture $2IrS_2.Ir_2S_3$. If the treatment with hydrogen sulphide takes place at 20°

to 30°, a smaller proportion of sesquisulphide is formed, and the mixture approximates $6IrS_2.Ir_2S_3$; and at 0°, a still larger proportion of disulphide is present in the mixture. Hence it is impossible by the wet method to prepare the disulphide without admixed sesquisulphide.

Iridium disulphide is variously described as a black, brown, or yellowish-brown powder. U. Antony said that moist air has no action on the product prepared in the dry way. L. N. Vauquelin observed that when the disulphide is roasted in air, iridium is formed; U. Antony said that this reaction occurs in air at 300°; and that the product is reduced to a lower sulphide when heated in carbon dioxide. L. R. von Fellenberg observed that at ordinary temp. chlorine does not decompose the product obtained in the dry way, but at a higher temp., sulphur chloride, and iridium chloride are formed. The sulphide resists attack by hydrochloric and nitric acids; it is decomposed by fuming nitric acid, and by aqua regia; it is not decomposed by boiling aq. ammonia, or by soln. of potassium hydroxide or sodium carbonate. H. G. Krall, and L. Wöhler and co-workers found that at 600°, iridium trichloride and sulphur at 600° form **iridium trisulphide,** IrS_3, which at 700°, in nitrogen, passes into the monosulphide.

J. J. Berzelius, and L. R. von Fellenberg observed that when a mixture of finely-divided iridium, potassium hydroxide, and sulphur is fused for some time, and the cold product extracted with water, a **potassium iridium sulphide** remains. According to F. Höchtlen, and K. A. Hofmann and F. Höchtlen, when a mixture of iridium trichloride and ammonium polysulphide is kept for a few months, brown, tetragonal octahedra of **ammonium iridium sulphide,** $(NH_4)_3IrS_{15}$, or $Ir(NH_4S_5)_3$, are formed. The axial ratio is $a : c=1 : 1.093$.

J. J. Berzelius,[2] and E. Uricoechea, thought that they had prepared **iridous sulphate,** presumably $IrSO_4.nH_2O$, by evaporating a soln. remaining after precipitating sulphide from a soln. of potassium chloroiridate. The brownish-green amorphous mass is soluble in water. The existence of this salt has not been confirmed. J. J. Berzelius, and E. Uricoechea also said that when recently precipitated iridium disulphide is digested in cold nitric acid, not sufficient to dissolve it completely, a greenish- or reddish-brown soln. of **iridium hemitrisulphate,** or **iridium sesquisulphate,** presumably $Ir_2(SO_4)_3.nH_2O$, is formed. L. Marino obtained this salt by crystallization from a soln. of the hydrated sesquioxide in dil. sulphuric acid, and in absence of air.

M. Skoblikoff, and W. Palmaer prepared **iridous sulphatodiammine,** $[Ir(NH_3)_2(SO_4)]$, by the action of sulphuric acid on the chloride. The orange-yellow crystals are soluble in water; the corresponding **iridous tetramminosulphate,** $[Ir(NH_3)_4]SO_4$, crystallizes in rhombic prisms which decompose on heating, and are easily soluble in water. W. Palmaer prepared **iridium chloropentamminosulphate,** $[Ir(NH_3)_4Cl]SO_4.2H_2O$, by the action of conc. sulphuric acid on the chloropentamminochloride; it forms pale yellow, monoclinic crystals, with the axial ratios $a : b : c=1.1984 : 0.74831$, and $\beta=84° \ 48\frac{1}{2}'$; the sp. gr. is 2·691 at 15°; and the mol. vol., 152·3. Similar chromic, cobaltic, and rhodium salts are known. One part of the anhydrous salt at 15° dissolves in 134·5 parts of water. E. Rosenbohm studied the magnetic susceptibility. He also prepared **iridium chloropentamminohydrosulphate,** $4[Ir(NH_3)_5Cl]SO_4.3H_2SO_4.3H_2O$, in pale yellow prisms. Similar chromic, cobaltic, and rhodium salts are known. W. Palmaer obtained **iridium bromopentamminosulphate,** $[Ir(NH_3)_5Br]SO_4.H_2O$, in yellow plates, by triturating the nitrate with an excess of sulphuric acid. M. Delépine and J. Pineau prepared **iridium chloropyridinotetramminosulphate,** $[Ir(NH_3)_4pyCl]SO_4$; and **iridium chlorobispyridinotriamminosulphate,** $[Ir(NH_3)_3py_2Cl]SO_4.3H_2O$; and M. Delépine, **iridium dichlorobispyridinodiamminosulphate,** $[Ir(NH_3)_2py_2Cl_2]_2SO_4$, and **iridium dichlorobispyridinodiamminohydrosulphate,** $[Ir(NH_3)_2py_2Cl_2]HSO_4$. A similar cobaltic salt is known. C. Claus prepared **iridium sulphatopentamminosulphate,** $[Ir(NH_3)_5SO_4](SO_4)_2$; **iridium nitritopentamminosulphate,** $[Ir(NH_3)_5(NO_2)]SO_4$, is obtained by treating the

corresponding chloride of the series with sodium sulphate; **iridium dinitritotetramminosulphate,** $[Ir(NH_3)_4(NO_2)_2]_2SO_4.\frac{1}{2}H_2O$, in acicular crystals, by decomposing the chloride with potassium sulphate or sulphuric acid; and **iridium dichlorotetramminosulphate,** $[Ir(NH_3)_4Cl_2]_2SO_4.H_2O$, in yellow leaflets, by triturating the corresponding chloride with conc. sulphuric acid. A. Werner and O. de Vries, and M. Skoblikoff also prepared this salt.

L. de Boisbaudran observed that when an iridium salt is fused at a dull red-heat with potassium hydrosulphate in a gold crucible for some minutes, either directly or after it has been evaporated with excess of sulphuric acid, until white fumes are given off, and, when the proportion of iridium is not too great, the residue dissolves completely in hot water, forming a solution which is usually green, but is sometimes blue or violet. Conc. soln. on cooling deposit **potassium sulphatoperiridite,** $K_3Ir(SO_4)_3$, as a green, crystalline powder. When deposited slowly from conc. soln., it forms small transparent crystals, which have no action on polarized light, and are apparently octahedra, flattened parallel with one of the faces. It dissolves in water or dil. sulphuric acid, but is insoluble in a sat. soln. of potassium sulphate, and in dil. alcohol. An acidic soln. of the salt is not altered by boiling; but if the soln. is nearly neutral, and especially if it contains a certain proportion of potassium sulphate, the green colour rapidly changes to a very pale rose tint, and potassium hydroxide or ammonia now precipitates the iridium in the form of an oxide, which dissolves in dil. sulphuric acid, forming a deep violet soln. With ammonia, the precipitation is incomplete. An excess of potassium hydroxide added to the green soln. in the cold changes the colour to pale blue, without any immediate precipitation; but on heating it, a rich violet colour is quickly developed, and the iridium rapidly separates out as a blue-violet oxide, soluble in dil. sulphuric acid; sometimes the colour produced by potassium hydroxide is violet-grey, and the precipitate is also violet-grey, but it yields the same rich violet soln. with dil. sulphuric acid. The green salt is not altered by dil. hydrochloric acid, nor by hydrochloric acid and iodine, but hot dil. nitric acid changes the colour to a somewhat feeble blue-violet. Aqua regia decomposes the salt completely with formation of iridium tetrachloride, and the sulphuric acid can be precipitated by barium chloride. If barium chloride is added to a soln. of the original salt, the precipitated barium sulphate has a deep green colour, and retains a considerable quantity of iridium, which is not removed even by aqua regia. A soln. of the green salt in dil. sulphuric acid acquires a pale blue-violet colour, when heated with potassium permanganate. If hydrochloric acid is previously added, the colour produced is very deep green. A hydrochloric acid soln. of the salt also acquires a deep green colour when heated with potassium chlorate. Sulphur dioxide has no action on a hot acid soln. of the salt.

M. Delépine obtained the *hydrate*, $K_3IrSO_4.H_2O$, in rectangular or hexagonal crystals, by boiling potassium or ammonium chloroperiridite for several hours with conc. sulphuric acid, and, after adding potassium sulphate, gradually raising the temp. to 520° to 530°; treating the solid product with cold water; dissolving the greenish-blue powder which remains in boiling water; and cooling the soln. This salt loses its water at 110°. An aq. soln. of the salt is completely or partially precipitated by adding various salt soln., and thus are formed the corresponding **rubidium sulphatoperiridite,** $Rb_3Ir(SO_4)_3$; **silver sulphatoperiridite,** $Ag_3Ir(SO_4)_3$; **strontium sulphatoperiridite,** $Sr_3\{Ir(SO_4)_3\}_2$; **mercurous sulphatoperiridite,** $Hg_3Ir(SO_4)_3$; **mercuric sulphatoperiridite,** $Hg_3\{Ir(SO_4)_3\}_2$; **thallous sulphatoperiridite,** $Tl_3Ir(SO_4)_3$; **thorium sulphatoperiridite,** $ThIr(SO_4)_3$; **bismuth sulphatoperiridite,** $BiIr(SO_4)_3$; **quinine sulphatoperiridite,** as well as **strychnine sulphatoperiridite.** The formulæ do not explain all the reactions of the salts. The precipitated salts have a bluish-green colour, and, as in the case of the potassium salt, the contained sulphuric acid is not precipitated by barium soln.; the barium salt, in fact, dissolves in acids without precipitation of any barium sulphate. Ammonia, and the alkali hydroxides and carbonates decompose these complex salts, and the

iridium is precipitated in the form of a violet-coloured oxide. The greenish-blue colour of soln. of the potassium salt is changed by reducing to a light yellow, but the addition of oxidizing agents converts the yellow into blue again. Barium sulphate is not precipitated from either the yellow or blue soln. on the addition of a soluble barium salt. A. Benrath and co-workers obtained **chromic hexamminosulphatochloroiridate,** $[Cr(NH_3)_6]_2(SO_4)_2(IrCl_6)$.

L. Marino observed that tervalent iridium sulphate, like the tervalent sulphates of rhodium, and cobalt, forms with the alkali sulphates a series of well-defined **iridium alums** which are isomorphous with the corresponding alums of aluminium, chromium, manganese, and iron. By concentrating in vacuo over sulphuric acid, a mixture of the theoretical proportions of soln. of ammonium sulphate, and iridium hemitrisulphate, yellowish-green octahedra of **ammonium iridium disulphate,** $NH_4Ir(SO_4)_2.12H_2O$, were obtained. The crystals melt at 105° to 106°, and at a higher temp. the combined water is expelled, and at a red-heat, iridium remains. F. Korten, and E. Rimbach and F. Korten, also prepared this alum. L. Marino similarly prepared **potassium iridium disulphate,** $KIr(SO_4)_2.12H_2O$, in yellow octahedra which begin to melt at about 96°, and are completely fused at 102° to 103°. The crystals are dehydrated in hot air, and the green or violet anhydrous salt remains soluble in water unless the temp. of dehydration exceeded 400°. At a red-heat, a basic sulphate and iridium are formed. L. Marino thus prepared **rubidium iridium disulphate,** $RbIr(SO_4)_2.12H_2O$:

A conc. soln. of iridium tetrachloride was reduced by the electric current yielding the trichloride which, on precipitation with potassium hydroxide free from alum, gave the hydrated hemitrioxide. The latter was thoroughly washed out of contact with the air and dissolved in the minimum quantity of dil. sulphuric acid. The calculated amount of rubidium sulphate was then added and the liquid evaporated in vacuo over sulphuric acid to furnish pale yellow octahedra.

The alum remains unaltered in air whether it be solid or in aq. soln. It melts at 108° to 109°. F. Korten, and E. Rimbach and F. Korten also prepared this alum. L. Marino also prepared **cæsium iridium disulphate,** $CsIr(SO_4)_2.12H_2O$, in a similar manner. The octahedral crystals melt at 109° to 110°. The aq. soln. is yellow at ordinary temp., but it becomes pink when warmed above 43°. F. Korten, and E. Rimbach and F. Korten also prepared this alum. L. Marino similarly prepared **thallous iridium disulphate,** $TlIr(SO_4)_2.12H_2O$, which forms golden-yellow octahedra.

According to J. J. Berzelius, a soln. of iridium disulphide in an excess of warm nitric acid yields a brownish-yellow soln. If conc. nitric acid be employed, the resulting **iridic sulphate,** or **iridium disulphate,** $Ir(SO_4)_2$, remains undissolved as a brown, amorphous mass, soluble in water, and in alcohol. The aq. soln. does not give a precipitate with alkali lye. When strongly heated it forms **iridium oxysulphate,** analogous to that obtained by roasting iridium sulphide. F. Korten, and E. Rimbach and F. Korten also prepared the disulphate as a yellowish-brown, amorphous mass, which, on heating with conc. sulphuric acid, becomes green hemitrisulphate. According to M. Delépine, iridic sulphate forms two series of salts which can usually be converted one into the other by the addition of an excess of acid to the basic salts, and of base to the acidic salts.

(1) *Acidic green salts of the type:* $R_2[Ir(SO_4)_2(H_2O)OH)]$.—These salts are all soluble in water, but less soluble in alcohol, ether, or a soln. of another salt of the same metal. When ammonium chloroperiridite is boiled with moderately conc. sulphuric acid, a yellow powder is obtained, which dissolves slowly in the acid, giving a green soln. If the soln. is mixed with an equal weight of water and left in the cold for some days, a mixture of star-shaped crystals and of rectangular needles separates out. The dark green, star-shaped crystals correspond with **ammonium iridium disulphate,** $(NH_4)H_3[Ir(SO_4)_2(H_2O)(OH)]_2$; and in aq. soln., this salt is transformed into $(NH_4)_3H[Ir(SO_4)_2(H_2O)(OH)]_2$, which crystallizes in dark green needles, soluble in 210 parts of water at 16°. This salt is also obtained

by adding a soln. of the more acid salt to a soln. of ammonium chloride or sulphate. The following salts were also obtained from the ammonium salts: **potassium ammonium iridium disulphate,** $K_8(NH_4)H_3[Ir(SO_4)_2(H_2O)(OH)]_6.3H_2O$, in green to black needles; **potassium iridium disulphate,** $K_4H_2[Ir(SO_4)_2(H_2O)(OH)]_3.1\frac{1}{2}H_2O$, in needles; $K_5H[Ir(SO_4)_2(H_2O)(OH)]_3.3H_2O$, in hexagonal or octahedral crystals; $K_2[Ir(SO_4)_2(H_2O)(OH)].H_2O$, in dark green, opaque, square crystals; $K_2H_4[Ir(SO_4)_2(H_2O)(OH)].6H_2O$, tetrahedral crystals, stable only in the presence of strong acids; **sodium ammonium iridium disulphate,** $Na_8(NH_4)H_3$-$[Ir(SO_4)_2(H_2O)(OH)]_6.18H_2O$, very soluble black crystals, almost rectangular; **thallous ammonium iridium disulphate,** $Tl_7(NH_4)_2H_3[Ir(SO_4)_2(H_2O)(OH)]_6$; **thallous iridium disulphate,** $Tl_7H_5[Ir(SO_4)_2(H_2O)(OH)]_6.6H_2O$, green needles, slightly soluble in water; **barium iridium disulphate,** $Ba_2H_2[Ir(SO_4)_2(H_2O)(OH)].12H_2O$; and **barium ammonium iridium disulphate,** $Ba(NH_4)[Ir(SO_4)_2(H_2O)(OH)].2H_2O$, in opaque, black octahedra.

(2) *Basic reddish-brown salts of the type:* $R_3[Ir(SO_4)_2(OH)_2]$.—If an excess of ammonia be added to a soln. of the green ammonium salt, the colour changes to reddish-brown, and on adding alcohol, an olive-brown salt, $(NH_4)_7H_2[Ir(SO_4)_2(OH)_2]_2$, is precipitated. An aq. soln. of this substance, when acidified, exhibits a green colour, and gives no precipitate with barium chloride. When heated at 100°, the substance loses one-seventh of its ammonia, and the colour changes from olive-brown to grass-green. The potassium salt, $K_7H_2(A''')_3,6H_2O$, crystallizes in needles varying in colour from old rose to blackish-brown, according to thickness. This salt is prepared by pouring a cold solution of the ammonium salt $NH_4H_3(A'')_2$ into excess of potassium carbonate solution. The sodium salt, $Na_7H_2(A''')_3,6H_2O$ and $9H_2O$, in reddish-brown clusters of needles or rectangular plates, is obtained by precipitation with alcohol. The **thallium ammonium hydroxydisulphate,** $Tl_{21}(NH_4)_7H_8(A''')_{12}$, and the **thallous hydroxydisulphate,** $Tl_7H_2(A''')_3,4\frac{1}{2}H_2O$, in dark brown crystals, are very slightly soluble. The **barium hydroxydisulphate,** $Ba_7H_4(A''')_6$,Aq., is a greenish-brown, amorphous precipitate, turning pure green on exposure to air and slowly depositing barium sulphate. A. Benrath also obtained a complex bromosulphate.

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§ 14. The Carbonates, Nitrates, and Phosphates of Iridium

No **iridium carbonate** has been prepared, but W. Palmaer [1] observed that when a soln. of iridium hexamminohydroxide is exposed to the air, a crust of **iridium hexamminocarbonate,** $[Ir(NH_3)_6]_2(CO_3)_3$, in microscopic, six-sided plates, is formed. C. Claus also obtained **iridium carbonatopentamminocarbonate,** $[\{Ir(NH_3)_2\}_2CO_3](CO_3)_2.3H_2O$, by the action of carbon dioxide on the corresponding hydroxide. M. Delépine prepared **iridium chloroaquobispyridinodiamminocarbonate,** $[Ir(NH_3)_2py_2(H_2O)Cl]CO_3.6H_2O$. A. Benrath also obtained a complex carbonate.

No **iridium nitrate** has been reported, but M. Skoblikoff prepared **iridous tetramminonitrate,** $[Ir(NH_3)_4](NO_3)_2$. W. Palmaer obtained **iridium hexamminonitrate,** $[Ir(NH_3)_6](NO_3)_3$, by the action of conc. nitric acid on the chloride. It is somorphous with the corresponding cobaltic, chromic, and rhodium salts. The tetragonal crystals have the axial ratio $a : c = 1 : 1{\cdot}042$; the sp. gr. is 2·395 at 15°, and the mol. vol., 201·0. At 14°, 100 c.c. of a sat. soln. contain 1·65 grms. of the salt. W. Palmaer prepared **iridium aquopentamminonitrate,** $[Ir(NH_3)_5(H_2O)](NO_3)_3$, by the action of nitric acid on the corresponding hydroxide. Similar chromic, cobaltic, and iridium salts are known. The white, microscopic plates have a sp. gr. 2·476 at 17°, and mol. vol., 195·9. When heated to 100°, it forms the nitratopentamminonitrate ; and detonate at a red-heat. At 17°, one part of the salt requires 10 parts of water for dissolution. The reaction: $[Ir(NH_3)_5(H_2O)](NO_3)_3 \rightleftharpoons [Ir(NH_3)_5(NO_3)](NO_3)_2 + H_2O$, is reversible in aq. soln. A. Werner and A. P. Smirnoff prepared the dextro- and lævo-forms of **iridium trisethylenediamminonitrate,** $[Iren_3](NO_3)_3$, the former with a sp. rotation of 42°, and the latter, −57·5°, for Na-light.

W. Palmaer observed that when the chloropentamminosulphate is treated with the theoretical quantity of barium nitrate, **iridium chloropentamminonitrate,** $[Ir(NH_3)_5Cl](NO_3)_2$, is formed in aggregates of yellow crystals. The sp. gr. is 2·404 at 15·5° ; and the mol. vol. is 182·1. Similar chromic, cobaltic, and rhodium salts are known. The salt does not lose weight at 100°, but it detonates at a red-heat. At 15°, 1 part of the salt dissolves in 51·5 parts of water. As just indicated, when iridium aquopentamminonitrate is heated to 100° it forms microscopic tetragonal plates of **iridium nitratopentamminonitrate,** $[Ir(NH_3)_5(NO_3)](NO_3)_2$. C. Claus also prepared this salt. According to W. Palmaer, the sp. gr. is 2·510 at 18·5° ; and the mol. vol. is 185·0. A similar cobaltic salt is known. B. E. Dixon prepared **iridium hydroxypentamminonitrate,** $[Ir(NH_3)_5(OH)](NO_3)_2$. At 16°, 100 c.c. of soln. contain 0·286 grm. of salt ; and he also obtained **iridium chloropentamminohydroxide,** $[Ir(NH_3)_5Cl](OH)_2.H_2O$. A. B. Lamb and L. T. Fairhall observed that the speed of conversion to the aquo-salt is in accord with a unimolecular reaction. Chlorine water colours the aq. soln. violet ; conc. hydrochloric acid precipitates tetragonal plates of **iridium nitratopentamminochloronitrate ;** nitric acid precipitates the unchanged nitrato-nitrate ; ammonium oxalate gives a white precipitate ; barium dithionate, a white crystalline precipitate ; sodium pyrophosphate, mercuric chloride, mercuric cyanide, and potassium ferrocyanide and ferricyanide give no precipitate ; gold chloride precipitates prismatic crystals ; and platinic chloride precipitates pale yellow, six-sided plates. A. Benrath and co-workers prepared **chromic hexamminonitratochloroperiridite,** $[Cr(NH_3)_6](NO_3)(IrCl_6)$; and **cobaltic hexamminonitratochloroperiridite,** $[CO(NH_3)_6](NO_3)(IrCl_6)$.

A. Werner and O. de Vries prepared the racemic form of **iridium dinitritobisethylenediaminonitrate,** $[Iren_2(NO_2)_2](NO_3)$; the dextro-form with a sp. rotation of 24·8°, and the lævo-form with a sp. rotation of −26·8° for Na-light.

M. Skoblikoff prepared an impure **iridic dichlorotetramminonitrate,** $[Ir(NH_3)_4Cl_2](NO_3)_2$.

J. J. Berzelius [2] heated iridium in phosphorus vapour, and roasted the resulting phosphide, and obtained an **iridium phosphate.** According to E. Uricoechea,

molten phosphoric acid dissolves a little finely-divided iridium, forming a pale green mass. It is uncertain whether the colour was not due to the presence of some osmium. All this is vague and indefinite. W. Crookes observed that fused phosphates had no effect on iridium.

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